CFTRI SCRC
2317
Foams Theory an

FOAMS:

THEORY AND INDUSTRIAL APPLICATIONS

by

J. J. BIKERMAN

in collaboration with

J. M. PERRI

Director of Research
National Foam Company

R. B. BOOTH

Mineral Dressing Laboratory
American Cyanamid Company

C. C. CURRIE

Manager, Fluids Section
Product Engineering Laboratories
Dow Corning Corporation

LIBRARY
18 JUN 1954

BOOK DIVISION
REINHOLD PUBLISHING CORPORATION
330 West 42nd St. New York 36, N. Y.

Also Publishers of Chemical Engineering Catalog, Chemical Materials Catalog, Materials & Methods—the Magazine of Materials Engineering; Advertising Management for American Chemical Society

1953

FReL2; 53
N53

2947

Copyright 1953 by
REINHOLD PUBLISHING CORPORATION

all rights reserved

Library of Congress Catalog Card Number: 53-8705

CFTRI-MYSORE
2947
Foams: Theory an..

Printed in U.S.A. by
THE WAVERLY PRESS, Inc.

PREFACE

This volume was written for scientists who intend to profit by foam, or are plagued by it, or, last but not least, are interested in foam just because foam is so interesting.

Preparation of a treatise on foam is a trying task. Froth has affected human lives ever since Aphrodite rose from the sea foam, long before physics and chemistry came into being. No laboratory is needed to observe foams, and the simplest of tools are sufficient to make observations on them. As a result, many a research on froth was carried out and recorded without due regard to the previous art; and the literature on foam is replete with repetitions and contradictions. A critical treatise on such a topic should prove useful. The authors have tried to bring some degree of order into the confusion of empirical practice, journal literature, and patent data, and thus to lighten the toil of future students, users, and fighters of foam.

The first part of the book (Chapters 1 to 11) deals with the fundamental knowledge of foams, and the second with their applications (Chapters 12 to 14) and inhibition (Chapter 15).

J. J. Bikerman

New York, N. Y.
August 15, 1953

LIBRARY
18 JUN. 1954

CONTENTS

Chapter		Page
1.	Formation and Structure of Foams	1
2.	Methods of Measuring Foaminess	27
3.	Results of Foaming Measurements	50
4.	Foam Drainage	98
5.	Mechanical Properties of Foams	114
6.	Optical Properties of Foams	137
7.	Electrical Properties of Foams	145
8.	Radius of Molecular Action. Black Spots	151
9.	The Theory of Foams	158
10.	Separation by Foam	171
11.	Three-phase Foams	184
12.	Fire-Fighting Foams *by J. M. Perri*	189
13.	Froth Flotation *by Robert B. Booth*	243
14.	Miscellaneous Uses of Foam	282
15.	Chemical Antifoaming Agents *by C. C. Currie*	297
	Author Index	331
	Subject Index	339

1. FORMATION AND STRUCTURE OF FOAMS

Section 1. Foams are agglomerations of gas bubbles separated from each other by thin liquid films. They belong to the first of the eight classes of colloidal systems listed below:

gas dispersed in liquid
liquid dispersed in gas (mist, fog)
liquid dispersed in liquid (emulsion)
gas dispersed in solid (solid foam)
solid dispersed in gas (smoke, fume)
liquid dispersed in solid (some gels)
solid dispersed in liquid (many sols and suspensions)
solid dispersed in solid

Other representatives of the first class, i.e., gas-in-liquid dispersions in which the liquid phase is not reduced to thin films, have been studied much less than foams (see section 8).

Section 2. Colloidal systems usually are prepared either by dispersion or by condensation (agglomeration). In the dispersion methods, the future disperse (or discontinuous) phase (i.e., gas in foam) is originally present as a large separate phase and is then comminuted and spread through the dispersion medium (also known as continuous phase) such as liquid in foam. In the condensation (or agglomeration) methods, the future disperse phase is originally present as solute, i.e., molecules or ions dissolved in the continuous phase; and in the process of preparing a colloidal system these molecules or ions combine to larger aggregates.

Blowing soap bubbles, injecting air into a frothing solution, whipping, and beating are instances of foam formation by dispersion. Foam on beer or a boiling liquid is produced by condensation.

Bubble Formation: Dispersion Methods

Section 3. One of the most important methods of dispersing gas in liquid consists in introducing gas bubbles into the liquid through

relatively fine orifices. This method is sometimes used in flotation and in the aeration of liquids. The simpler case of a single orifice will be considered first.

When a bubble forms above the orifice of a capillary, the buoyancy, which tends to raise the bubble and thus to separate it from the main body of gas, is $\frac{4}{3}\pi R^3 g\rho$. In this expression R is the radius of the bubble or, if the bubble shape is too far from that of a sphere (the bubble is never exactly spherical), the radius of the sphere having the volume of the bubble; g is acceleration due to gravity (for which the value 981 cm sec^{-2} is accepted in this book); and ρ is the difference between the densities of liquid and gas; usually ρ practically coincides with the density (g cm^{-3}) of the liquid. The force of buoyancy is counteracted by surface tension γ (measured in dynes/cm or ergs/cm^2 or g sec^{-2}) acting along the perimeter of the neck of the bubble. The length of this perimeter seems to be a complicated function of the apparatus dimensions and of the properties of the gas and the liquid; this problem has been thoroughly examined for the instance of falling drops (see e.g., ref. 1, p. 15). As a first approximation the neck perimeter is set equal to the circumference of the orifice, if the capillary is wetted by the liquid. Denoting the inside radius of the capillary by r, this approximation would require the bubbles to loosen themselves from the capillary as soon as $\frac{4}{3}\pi R^3 g\rho$ becomes greater than $2\pi r\gamma$, i.e., when R^3 just exceeds the value given by the equation

$$R^3 = \frac{3r\gamma}{2g\rho}. \tag{1}$$

If the capillary is not wetted by the liquid (e.g., a waxed capillary in water), r in equation (1) is the outside radius.

For liquid drops slowly falling from a capillary it is found that R^3 is smaller than $3r\gamma/2g\rho$. The ratio $2R^3 g\rho/3r\gamma$ (a pure number) usually varies between 0.52 and 0.65. For bubbles slowly forming in a liquid, equation (1) correctly represents the dependence of R^3 on r, γ, and ρ, but the ratio $2R^3 g\rho/3r\gamma$ varies within wider limits than in the instance of drops (see also section 10).

Maier[2] found the above ratio to be unity for air bubbles separating from glass capillaries in water when r varied from 0.0007 to 0.0112 cm. When a waxed capillary was used, the bubble radius R was almost three times as great as in the case of a glass capillary; R has not been compared with the outside radius. Apparently, as long

as the capillary is wetted by the liquid, the material of the capillary wall is irrelevant[3].

The upper part of Table 1 shows some results obtained by Guyer and Peterhans[4] and recalculated by the present author. The lower part of the table is a similar selection of data from a paper by van Krevelen and Hoftijzer[5]. It is seen that the ratio $2R^3g\rho/3r\gamma$ may be as low as 0.59 and as high as 1.05. Values as high as 1.9 have been recorded in the literature[5a]. When the nozzle is horizontal rather than vertical, bubble volume is only half as large[5a].

TABLE 1. DIAMETER OF AIR BUBBLES RISING FROM AN ORIFICE (GLASS)

Orifice diameter: $2r$ cm. Bubble diameter: $2R$ cm. Ratio: $2R^3g\rho/3r\gamma$. Water: $\rho = 1.00$ g cm^{-3}, $\gamma = 72$ g sec^{-2}. Carbon tetrachloride: $\rho = 1.58$ g cm^{-3}, $\gamma = 26$ g sec^{-2}. Ether: $\rho = 0.71$ g cm^{-3}, $\gamma = 16$ g sec^{-2}.

	Water		CCl_4		Ether	
$2r$	$2R$	Ratio	$2R$	Ratio	$2R$	Ratio
0.0045	0.125	0.98	0.065	0.61	0.075	0.68
0.008	0.150	0.96	0.085	0.76	0.090	0.66
0.032	0.220	0.60	0.135	0.76	0.145	0.69
0.100	0.325	0.78	0.190	0.68	0.215	0.72
0.264	0.410	0.59	0.270	0.74	0.280	0.61

Water: $\rho = 1.00$, $\gamma = 72$. Transformer oil: $\rho = 0.877$, $\gamma = 35$.

	Water		Transformer Oil	
$2r$	$2R$	Ratio	$2R$	Ratio
0.15	0.39	0.90	0.318	0.88
0.95	0.76	1.05	—	—

The ratio $2R^3g\rho/3r\gamma$ seems to be nearly independent of temperature[6a]. Thus for air bubbles rising in water from a glass capillary, 0.293 cm in diameter, it was 0.945 at 13° and 1.036 at 60°. However, the bubble volume was even better constant, namely 0.0652 cm^3 at 13° and 0.0655 cm^3 at 60°. When density was raised without markedly affecting surface tension (by using a concentrated zinc chloride solution, $\rho = 1.486$) or when surface tension was lowered more than density (by using water-alcohol mixtures), the above ratio still remained almost equal to unity[6a]. In other experiments[5a] bubble volume varied as γ/ρ when small orifices were used but was almost independent of the concentration of alcohol (in its aqueous solutions) for large orifices. As would be expected, the radius of bubbles slowly forming at a single orifice was independent of viscosity (in glycerol-water mixtures)[5a]. When surface tension was lowered by a commercial detergent ("Teepol," a sulfonated secondary alcohol), the bubbles were greater than calculated from equation (1) presumably because

the detergent was concentrated in the upper surface of the solution while the lower strata, in which bubble formation took place, contained but little of the surface-active compound[6a].

Section 4. The bubbles recorded in the upper part of Table 1 were produced one every second, and the bubbles of the lower part every 0.7 to 3 sec. When the frequency of the bubble discharge is considerably greater, equation (1) ceases to be valid even semiquantitatively and R becomes dependent, in addition to r, γ, g, and ρ, also on this frequency and on the viscosity η of the liquid.

According to Maier[2], increased rate of air flow affects the maximum size of bubbles in two opposite ways. The more rapid the introduction of air, the stronger is the agitation of the liquid, which tends to tear away the bubble before it is big enough to rise of itself. On the other hand "the excess pressure or viscosity effect" causes increase of R with the rate of flow. This second effect, known also for falling drops, seems to consist in the following. Contraction of the bubble neck is the first stage in the separation of the bubble. This contraction takes time, which may be expected to be longer the more viscous the liquid. During this time the air continues to flow into the bubble; hence the final bubble is greater than expected.

Overlapping of these two effects may cause a minimum of R at some velocity of air (V cm^3/sec). Maier found indications of such minima for air bubbling into water from glass capillaries; the volume velocity V corresponding to the minimum or R increased with the radius of the orifice. Analogous observations have been made by Datta *et al.*[5a] for orifices smaller than 0.04 cm in diameter, while the radius of bubbles rising from larger orifices was almost independent of V. In the similar experiments by Remy and Seemann[6], at $V = 16$ cm^3/sec, R passed through a minimum when the orifice diameter increased.

The velocity V is equal to $n \cdot 4\pi R^3/3$, if n is the number of bubbles produced in a second, and the value of R can be correlated either with V or with n. Fig. 1, which is based on some data published by Guyer and Peterhans[4], is an example of such correlations. Its ordinate is bubble diameter, and along its abscissa are plotted (below) the number n (sec^{-1}) and (above) the rate of air flow. The air flow curve is shown for castor oil only because the highest air rate employed for olive oil was 0.06 cm^3/sec and for carbon disulfide as low as 0.015

cm^3/sec. Fig. 1 thus shows that the effect of n on R is greater the more viscous is a liquid (castor oil has η of 9.5, olive oil 0.84, and carbon disulfide 0.0035 g/cm sec). However, it does not give sufficient information on how the relation between V and R is affected by vis-

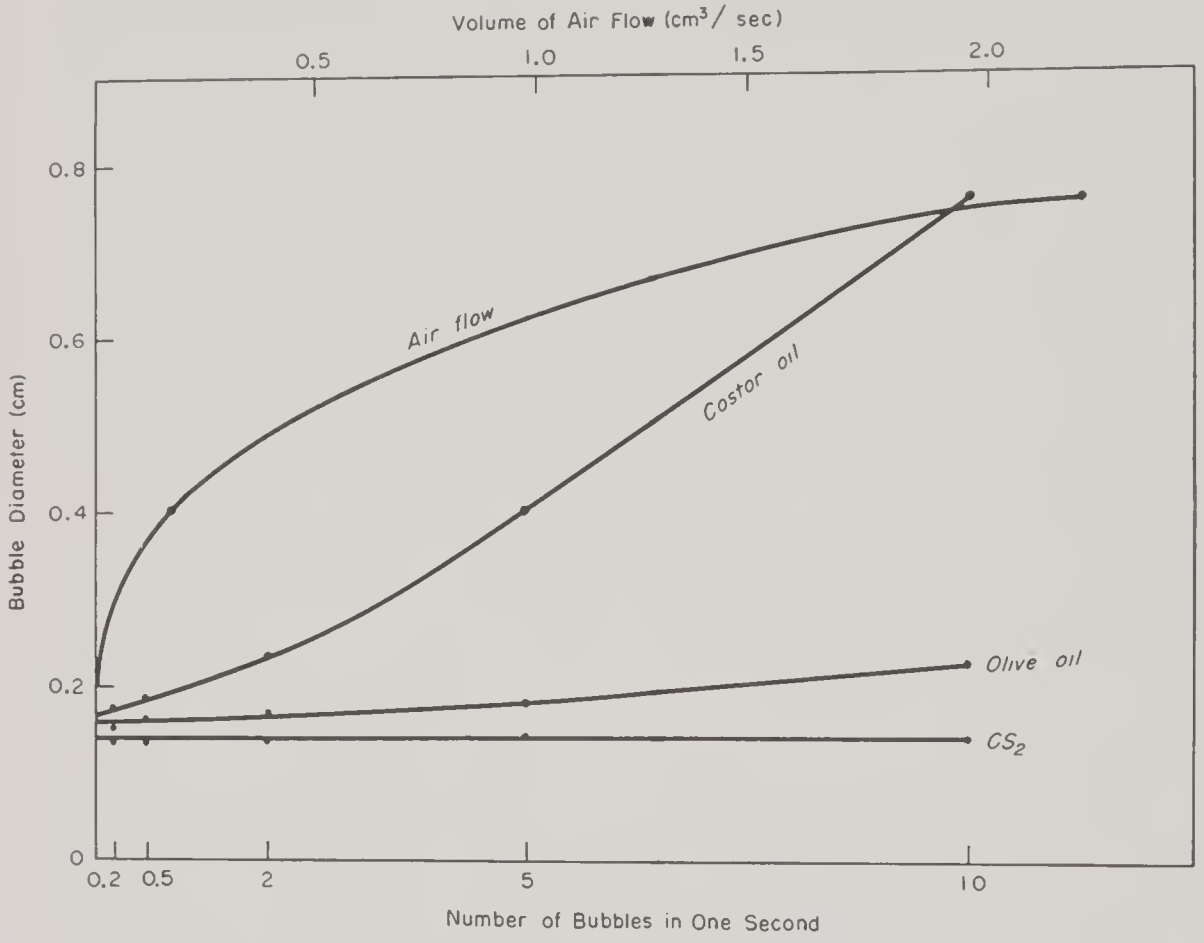


FIGURE 1. Dependence of air bubble diameters on the bubble frequency and the rate of air flow. The lower scale is for the curves marked castor oil, olive oil, and CS_2. The upper scale is for the "air flow" curve which refers to castor oil; to obtain the linear rate of air flow, multiply the figures of this scale by 2,630 $cm.^{-2}$. Data of Guyer and Peterhans[4].

cosity because the high velocities used in the instance of castor oil were not tested for the less viscous liquids.

The relation between bubble volume and rate of gas flow in water was a little different for different capillaries. However a common curve resulted when the ratio $2R^3g\rho/3r\gamma$ was plotted as a function of the number of bubbles per minute; the ratio was nearly independent of n at small n and increased with n at large n. It was impossible to produce more than about 40 bubbles in a second[6a].

Remy and Seeman[7] found that in ether the bubble volume was

independent of V within the range of 0.8–3.3 cm^3/sec. In ethyl alcohol it increased from 0.18 to 0.56 cm^3 when V increased from 0.8 to 16 cm^3/sec.

Instead of the volume velocity V, the linear velocity $V/\pi r^2$ may be correlated with R. The range of linear velocities for which Guyer and Peterhans (see Fig. 1) found R independent of V in the instance of carbon disulfide was 7 to 40 cm/sec; the diameter of the orifice was 0.022 cm. In water, when the volume rate of air increased from 4.17 to 38.3 cm^3/sec and the linear velocity from 370 to 3400 cm/sec, the bubble diameter increased from 0.613 to 1.483 cm and the frequency of bubbles *decreased* from 35 to 23 sec^{-1}.

It is clear that the experimental material available is not sufficient to decide whether the bubble volume should be correlated preferably with volume rate, linear rate, or frequency. It is also impossible to state how an increase of the product nR^3 (i.e., also of V) is distributed between n and R.

Eversole, Wagner, and Stackhouse[8] observed that the bubble frequency was about 40 to 50 sec^{-1} for different liquids, different capillaries, and different air rates.

Van Krevelen and Hoftijzer[5] point out that the volume of bubbles at high air rates is determined by the condition that two succeeding bubbles should not touch. If the air is transported by a chain of bubbles, n in a second, the height of this chain produced in a second must be greater than $n \cdot 2R$, assuming the bubbles to be spherical. On the other hand, the height of a bubble chain produced within a second is the linear ascending velocity u of the bubbles. It follows that $u > 2nR$ or $R^2 < 3V/2\pi u$ (as $V = \frac{4}{3}\pi R^3 n$). Application of this formula is not easy, however, as the value of u in a liquid periodically disturbed by new bubbles has not been calculated yet, although some progress has been achieved by application of the dimensional analysis[5]. The above assumption of spherical bubbles is not justified for well frothing liquids. In these, two bubbles can be pressed against each other and thus be greatly deformed without coalescence (see the two-bubble method in Section 19 and Pattle[8a]).

Section 5. In sections 3 and 4, bubble formation at single orifices was discussed. When several orifices are placed so near each other that bubbles growing at them can coalesce, the diameter of the bubbles ceases to be proportional to the r of the orifice. For example,

when $2r$ in sintered glass plates increased from 10 to 65 μ (i.e., from 0.001 to 0.0065 cm), $2R$ in water increased, depending on the air rate, only from 0.05 to 0.11 or from 0.19 to 0.23 cm. The bubble diameter rose also with V and was almost independent of viscosity[5]. On the contrary, Schnurmann[9] observed a minimum of R in water-alcohol mixtures just at the concentration corresponding to the maximum in viscosity and maintained that R of bubbles produced by coalescence depends on viscosity more than on anything else.

In some instances correlation seems to exist between the average bubble radius and the surface tension γ of the solution in which the foam is produced by forcing air through a porous plate[10]. Table 2 shows the γ, the most frequent R, the surface S of all the bubbles in 1 cm^3 of the foam, and the product γS for five concentrations of sodium 6-butylnaphthalene-1-sulfonate in water. The product γS, i.e., the

Table 2. Effect of Concentration of Sodium 6-Butylnaphthalene-1-Sulfonate on Bubble Size

Concentration (%)	2	0.5	0.25	0.125	0.06
Surface tension (γ g sec^{-2})	30	32	38	52.5	60
Most frequent radius (10^{-4} cm)	80–90	90–100	100–110	100–110	120–130
Surface in 1 cm^3 (S cm^{-1})	360	330	270	250	210
$\gamma S \times 10^{-2}$	108	107	103	132	126

work against the surface forces spent in producing 1 cm^3 of foam, is almost independent of concentration. As $S = 3/R$, this rule can be expressed also by the statement that the maximum bubble pressure (which is approximately $2\gamma/R$) is almost independent of the concentration of the frother.

Formation of bubbles at gas diffuser stones[11] seems to have never been investigated.

Section 6. Generally speaking, injection of air produces *small* air bubbles when (see equation 1) the liquid has great density and small surface tension, and the orifice is narrow; also the gas flow should preferably be slow. However, when a finely dispersed foam (i.e., a foam consisting of small bubbles) is wanted, usually the properties of the liquid are given and cannot be altered at will; and reduction of the orifice diameter and the gas velocity would entail an unwelcome retardation of the formation of foam. It is clear that some other expedient is needed if small bubbles are to be obtained at a sufficient

rate. The device usually resorted to is production of bubbles in a *moving* liquid which tears them away before they reach their "natural" dimensions.

Maier[2] forced air through orifices (e.g., of 0.04 cm) in a drum which could be made to rotate between stationary vanes. When the drum did not move, these orifices gave rise to bubbles 0.35 to 0.4 cm in diameter, but when the drum made 1,700 revolutions per minute the bubble diameter was about 0.04 cm, i.e., roughly equal to the diameter of the orifices.

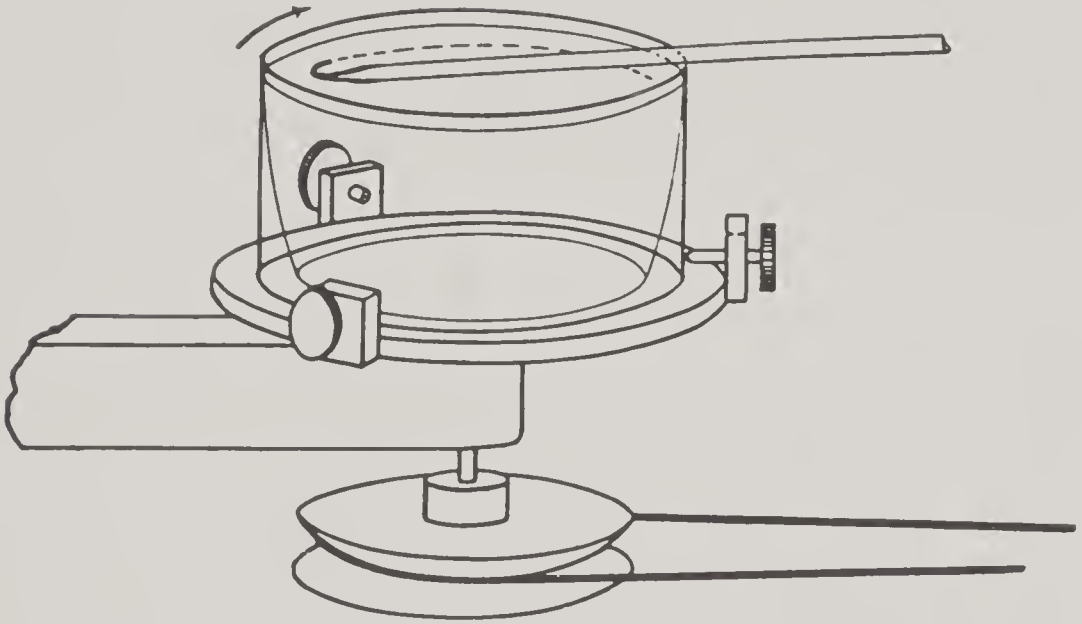


FIGURE 2. Apparatus for producing small bubbles. From *Proc. Roy. Soc.* (*London*), **190A**, 474 (1947).

Bragg and Nyc[12] applied pulling rather than shearing force. Their apparatus is shown in Fig. 2. The vessel containing the foaming solution was rotated, and air was introduced through a fine jet placed along the lines of flow. The bubbles were swept away by the moving liquid. Over 1,000 bubbles could be produced in a second, and the apparatus gave "a high pitched note." An orifice, 0.0038 cm across, fed by air compressed to 190 cm of water and placed in a liquid stream of 180 cm/sec, yielded bubbles of 0.014 cm in diameter.

Smith[13] used a double nozzle delivering air into a moving soap solution. When air was forced through a 0.0085-cm orifice by a pressure of 50 cm of water, the bubbles had diameters of 0.058 cm when the soap solution was driven by a 9-cm head, and 0.024 cm when the head was 100 cm.

Pattle[8a] placed a curved solid right above the orifice. The bubbles were deflected by the solid and escaped much earlier than in an unobstructed liquid. Bubbles of 0.00001 to 0.001 cm^3 were thus produced at rates from 100 to 2,000 per second.

Very small bubbles were obtained when a liquid capable of frothing was separated from air by a plate containing a fine orifice (e.g., 0.008 cm in diameter), and the air was under a sufficiently high pressure (more than 2 atmospheres)[13a]. Centripetal force apparently has not been tried out yet.

A recognized method of decreasing bubble diameter in a foam consists in forcing the froth through a sieve or screen. Presumably the action of the sieve is essentially identical with that of a porous plate or, if the holes in the sieve are relatively far apart, with that of single orifices. No information could be found on the relation between the final bubble volume on one hand and the initial volume, the hole diameter and the distance between the holes on the other hand.

Section 7. The process of introducing air bubbles into a liquid by whipping, beating, etc., undoubtedly is very complicated and, apparently, has not yet tempted any physicist. Several observations have been published on formation of bubbles by splash, i.e., by impact of a solid onto a liquid surface. The paper by Gilberg and Anderson[14] gives an idea of the complexity of the phenomena taking place.

An unusual kind of bubbles produced by splash has been observed by Melsens[15]. He directed a water jet onto a mercuy surface under a water layer so that air was mixed with mercury. The air bubbles enclosed in a mercury film rose through the water and floated on its surface. The largest bubbles had diameters of 1.5 cm and contained 0.5 g mercury (see also section 19).

The bubbles originally produced by whipping, etc., as well as by forcing air into a solution through a wide tube (as in many industrial aerations) usually are then broken to smaller bubbles by the continuing agitation. This effect has been observed also in emulsions and is relatively well understood (see, e.g., ref. 1, p. 145). A fluid cylinder, because of surface tension, tends to break and to give rise to two spheres when the length of the cylinder is greater than its circumference[16]. When an air bubble elongated by shearing forces (caused by the stirring) accidentally reaches a relatively stagnant part of the

liquid, it is likely to break into two or more spherical bubbles according to the ratio of its length to its circumference.

Devices for producing foam on a large scale are not discussed here because they have not been scientifically investigated. Some froth-making appliances used in ore dressing are described in Chapter 13. A recent publication by Fry and French[16a] will give an idea of the machines producing fire-fighting foams (see Chapter 12). In this machine air and the liquid capable of foaming enter a mixing chamber through nozzles in two opposite walls. The same pressure is employed to drive both fluids. All liquid entering the chamber is transformed into froth, that is, the ratio of air to liquid in the foam is identical with that in the mixing chamber. Before leaving the machine the foam passes through an "improver" consisting of gauze discs (see section 6).

Bubble Formation: Condensation Methods

Section 8. Formation of bubbles in a supersaturated solution of a gas in a continuous liquid is highly improbable. Two of the possible demonstrations will suffice to show the truth of this statement.

(a) A bubble whose radius is R has surface of $4\pi R^2$, and work equal to $4\pi R^2\gamma$ against the surface tension γ must be performed to make this bubble. The amount of gas in the bubble is $\frac{4}{3}\pi R^3\rho_0$, ρ_0 being the gas density. If the release of free energy, achieved when 1 g of gas is transferred from supersaturated solution into the bubble, is F, this for one bubble is $\frac{4}{3}\pi R^3\rho_0 F$. Spontaneous gas evolution is possible only as long as this term is greater than $4\pi R^2\gamma$, i.e., as long as $R\rho_0 F > 3\gamma$. It is clear, however, that whatever (within reason) the values of ρ_0, F, and γ, the product $R\rho_0 F$ is less than 3γ if R is sufficiently small. In other words, extremely minute bubbles cannot form. As bubbles must be minute before they can grow large, no bubbles can form spontaneously.

(b) By Laplace's equation the gas pressure in a bubble whose radius is R is by $2\gamma/R$ greater than the pressure in the surrounding liquid. The supersaturated solution would be in equilibrium with gas under a pressure, say, P and would tend to lose gas to a gas space in which the pressure is $<P$. Thus, a bubble can grow only if

$$\frac{2\gamma}{R} < P \tag{2}$$

If R is sufficiently small, this condition can be satisfied by improbably

great values of P only. Again, minute bubbles (and hence also large bubbles) cannot form spontaneously.

The probability of bubbles forming spontaneously in a superheated liquid (containing no dissolved gas) is even smaller. In this instance P would mean the vapor pressure of liquid in equilibrium with a bubble whose radius is R. According to W. Thomson (Lord Kelvin) (see, e.g., ref. 1, p. 56),

$$P = P_0 - (m \cdot 2\gamma/R), \tag{3}$$

m being the ratio of the density of the steam to the difference between the densities of liquid and steam, and P_0 the equilibrium vapor pressure at a plane surface. Bubbles can grow only if $2\gamma/R < P_0 - (2\gamma m/R)$, i.e., if $\frac{2\gamma}{R}(1 + m) < P_0$. As m is always positive, P_0 must be greater than P in formula (2). Thus, spontaneous boiling appears possible only at temperatures at which γ is negligibly small.

Bubbles can be obtained in liquids originally containing no gas nuclei by mechanically rupturing the liquid. Such a rupture can be achieved, e.g., by vortices[17], by rapidly moving a solid (preferably poorly wetted by the liquid) in a liquid[18], by collision of two solids in a liquid[19], and so on. However, liquids not subjected to special treatment as a rule contain small gas bubbles or dust particles carrying adsorbed gases, which both act as nuclei for larger bubbles. A more precise description of these nuclei is so far impossible[20].

Foam produced by releasing gas from a supersaturated solution is mentioned by Krause and Kapitańczyk[21]. They mixed, for example, 1 cm^3 of water saturated with nitrogen and 10 cm^3 of 19N sodium hydroxide. As nitrogen (and many other inert gases) is more soluble in water than in concentrated sodium hydroxide solution (and many other solutions of electrolytes), the resulting solution was supersaturated and yielded bubbles; their diameter was about 10^{-6} cm. When five drops of 30 per cent hydrogen peroxide were added to 20 cm^3 of 19N sodium hydroxide, the oxygen bubbles formed often combined to "flakes" of foam distributed in the liquid. The diameter of these bubbles was between 0.1 and 0.2×10^{-4} cm. Particularly small bubbles have been observed by Kapitańczyk[22] on adding 18N sodium hydroxide to a saturated solution of helium in water.

Section 9. Of greater importance is bubble formation in contact with a solid wall. This occurs particularly in boiling and in electrolysis.

De Luc in 1772, Schönbein in 1837, and Gernez[23] in 1875 expressed the opinion that solids act as nuclei in boiling simply because they contain dissolved or adhering air. Their hypothesis is borne out by recent observations. All the solids which caused release of dissolved air in water placed in a partial vacuum ceased to be active after an appropriate treatment aimed at removing the occluded air; in many instances (fibrin, rubber, etc.) nothing more drastic was required than to keep the solid for a while in de-gassed water.[17] As long as no precautions are taken to eliminate the occluded gases, no definite correlation can be found between the degree of superheat possible in the presence of a solid and the other properties of this solid[24].

It is often believed that rough surfaces promote boiling. This effect may be due not to the roughness as such but rather to the difficulty of removing occluded gases from a rough surface. Both Dean[17] and Larson[24] introduced rough solids into supersaturated air solutions in water and into water heated to boiling temperature, respectively, without causing any evolution of bubbles.

In many instances usual cleaning of solid surfaces does not remove all sources of gas nuclei, but only reduces their number. It is a common observation that boiling in contact with cleaned solids often originates from a few points. The number of these points increases with the temperature of the heating surface[25]. Thus, when 7500 kg-cal./sq m $\times$ hour were supplied to a horizontal polished metal surface in water, steam bubbles rose from five places only; and when 30,000 kg-cal./sq m $\times$ hour were supplied, 24 spots gassed.

Section 10. At a right temperature, wherever there is a gas nucleus, a steam bubble forms. As in section 3 it may be asked what determines the maximum size of a bubble just before it breaks loose. The following treatment is more exact than that leading to equation (1). In Fig. 3 a bubble sitting on a horizontal solid surface is depicted. At the level 00 the hydrostatic pressure in the liquid is P. In the bubble, at its summit, i.e., at the same level 00, the pressure is $P + \gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$, if γ is surface tension and R_1 and R_2 are the main radii of curvature at the summit. (This is again Laplace's law of capillary pressure, see section 8.) At a level such as MM, z cm below 00, the hydrostatic pressure is $P + gz\rho$ in the liquid whose density is ρ.

In the bubble at M it is $P + gz\rho + \gamma\left(\frac{1}{R_3} + \frac{1}{R_4}\right)$, R_3 and R_4 being the main radii of curvature at point M. On the other hand, the pressure in the bubble at M must be equal to the pressure at the summit plus the pressure of the gas above the level MM, i.e., to $P + \gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) + gz\rho^1$, if ρ^1 is the gas density. Hence,

$$gz(\rho - \rho^1) = \gamma\left(\frac{1}{R_1} + \frac{1}{R_2} - \frac{1}{R_3} - \frac{1}{R_4}\right) \tag{4}$$

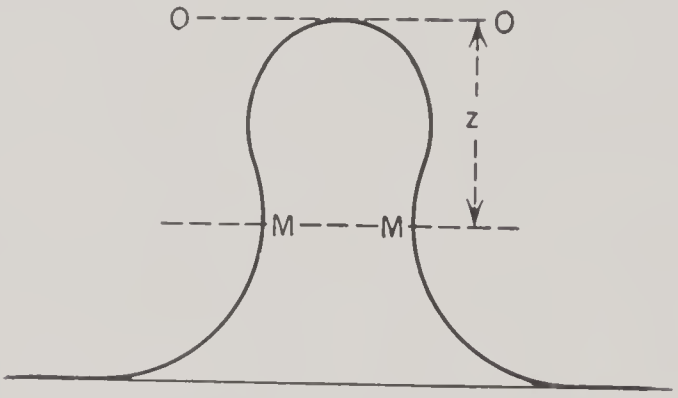


FIGURE 3. A sessile bubble. If the outside pressure at M is greater than the inside pressure, the neck at MM contracts, and a free bubble forms.

As bubbles are supposed to be symmetrical about the vertical axis passing through the summit, $R_1 = R_2$. Then, neglecting ρ^1 in comparison with ρ, we obtain

$$\frac{gz\rho}{\gamma} = \frac{2}{R_1} - \frac{1}{R_3} - \frac{1}{R_4} \tag{5}$$

If this equation is not satisfied, if at point M the pressure outside is greater than that inside the bubble, then the indentation at M will deepen and the bubble will eventually be separated from the solid.

Unfortunately the mathematical relation between the four lengths z, R_1, R_3, and R_4 is so complicated that no equation for the bubble contour can be given. The function $x = f(z)$, in which x is the radius of the horizontal section of the bubble z cm below the summit, has, however, been calculated by Bashforth and Adams[26] for several numerical values of the magnitude $g\rho R_1^2/\gamma$. If the bubble is submerged in water of 20°, i.e., ρ and γ are 1 g/cm^3 and 73 g/sec^2, respec-

tively, then this quantity is 13.4 R_1^2 cm^2. Fig. 4 represents vertical cross sections of such bubbles, drawn by Wark[27]. B in the graph is equal to $-g\rho R_1^2/\gamma$, and the contours for B = − 0.1 and −0.2 are incomplete because Bashforth and Adams' calculations are incomplete also. As an example, B = −0.1 corresponds to R_1 = 0.086 cm in water at 20°. Both z and x are in cm.

If a horizontal solid surface is present, say, 0.6 cm below the summit of a bubble, the shape of the sessile bubble is that shown by a contour above the line of z = 0.6. The angle formed (*in the liquid*)

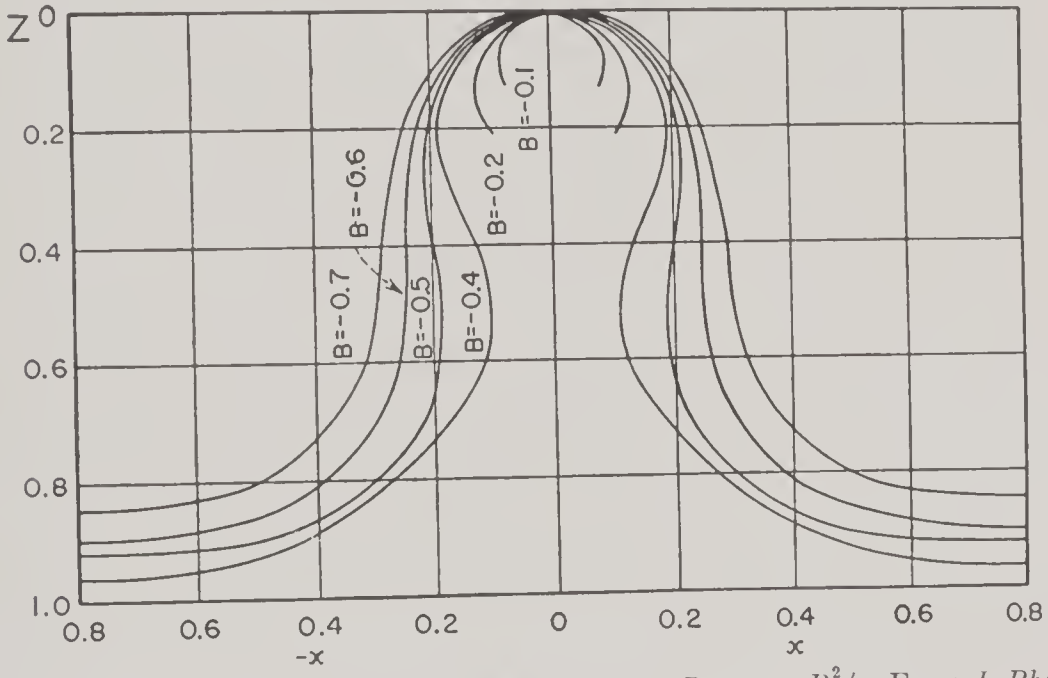


FIGURE 4. Outlines of sessile bubbles at different $B = -g\rho R_1^2/\gamma$. From *J. Phys. Chem.*, **37**, 623 (1933).

by the solid-liquid and the liquid-gas interfaces is the *contact angle* θ. Thus, if a bubble having B = −0.4 sits on a solid situated 0.4 cm below the summit, the contact angle is acute, whereas if the bubble is 0.6 cm tall, the contact angle is obtuse. The range of contact angles possible for a bubble depends on the latter's B. For example, a bubble having B = −0.4 can make an acute angle with a solid, but bubbles characterized by B = −0.7 cannot; their outline is everywhere inclined toward the gas phase. Thus it is possible to find the largest bubble (i.e., the largest −B) which still can make a given θ; e.g., the greatest −B for which θ = 90° is possible is not far from −B = 0.6, as the contour whose B = −0.6 seems still to show a stretch parallel to the ordinate, while for B = −0.7 no such stretch is discernible.

Fig. 5, taken from Jakob[25], shows that the greatest possible bubble volume v increases with θ so that $v^{1/3}$ (or the radius of the sphere of equal volume) is approximately proportional to θ up to $\theta = 100°$. In Fig. 5, θ is plotted along the abscissa, and the ordinate represents, rather than $v^{1/3}$ itself, the dimensionless ratio $\frac{v^{1/3} g^{1/2} \rho^{1/2}}{(2\gamma)^{1/2}}$ or $v^{1/3}/a$, a being Laplace's capillary constant equal to $(2\gamma/g\rho)^{1/2}$. This ratio is, of course, closely related to $-B$. For water at 20°, $a = 0.386$ cm and $v^{1/3}$ is approximately 0.0046 θ cm if θ is in degrees. Wark[27] calcu-

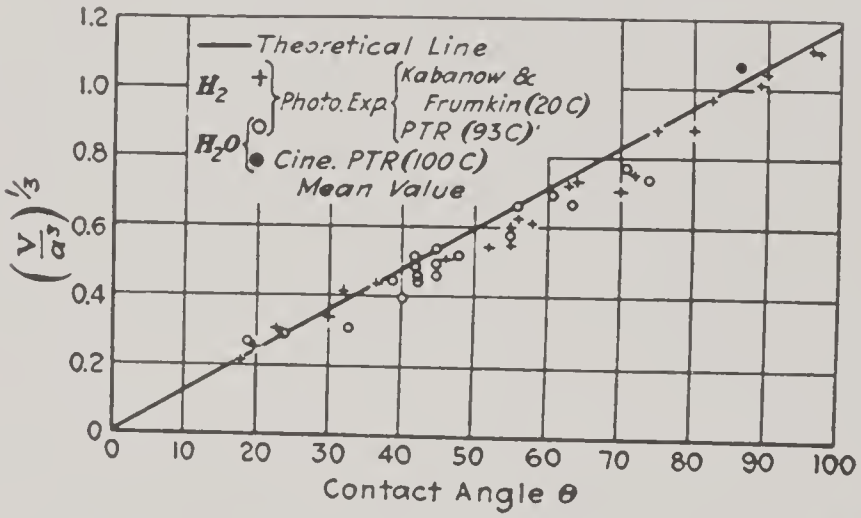


FIGURE 5. Relation between maximum volume of bubbles and contact angle. Abscissa: contact angle in degrees. Ordinate: $v^{1/3}/a$; v is the maximum volume of a bubble, a is Laplace's capillary constant. From *Mech. Eng.*, **58**, 643 (1936).

lated the maximum values of v for greater θ values also and found, for example, $v = 0.20$ cm^3 at $\theta = 130°$. In Fig. 5 also some experimental values of $v^{1/3}/a$ are inserted. The measurements have been carried out either in Jakob's laboratory or by Kabanov and Frumkin[28].

Section 11. The bubbles for which Fig. 4 and Fig. 5 are valid are in equilibrium: the calculation is based on the assumption that the two opposite forces cancel. The bubbles which actually rise from a horizontal solid surface and eventually become foam bubbles do not belong to an equilibrium system. They are always smaller than the largest possible bubbles. There are two main causes for this difference. (a) When a bubble grows it gradually displaces liquid from the solid surface. When a liquid-gas boundary moves along a solid, it

does not form the equilibrium contact angle θ. If liquid displaces gas, the angle formed (the *advancing* contact angle θ_A) is always greater than θ, and when gas displaces liquid, the *receding* contact angle θ_R is always less than θ. A θ_R determines the angle between a growing bubble and the solid surface. It follows then from Fig. 5 that the greatest possible bubble, when growing, is smaller than the equilibrium bubble. The importance of θ_R (rather than θ) for bubble formation apparently escaped the attention of the students of boiling. (b) When a bubble breaks loose, not all the gas present in the sessile bubble escapes. Without any calculation everyone inspecting Fig. 4 would expect, for example, bubbles whose $B = -0.4$ to "neck down" at about $z = 0.5$ cm and to leave the bottom part adhering to the solid. The relation between the volumes of hanging and fallen drops has been much discussed but no final result achieved. Even less is known concerning the relation between the analogous bubble volumes. If the rate of growth of steam bubbles is not very small, a third cause is operative: a bubble may be torn off before it reaches its limiting volume by waves produced by previous bubbles (see section 4 and below).

The nature of the solid surface from which a bubble rises affects the bubble volume insofar as it affects θ_R. Generally speaking, θ_R is greater the greater the equilibrium contact angle θ and the smoother the solid. Hence, the maximum bubble volume should increase with θ and with smoothness. This has been observed on many occasions. In Jakob's experiments on boiling of water, steam bubbles had a bell shape and reached diameters of 0.8 cm before detaching when the solid was oiled (large θ). On a smooth metal surface bubbles were like inverted pears, and on an indented metal surface they stood like eggs on end. The difference between the bubble shapes on smooth and rough surfaces cannot be due to any difference in the equilibrium contact angles as these angles between metal, water, and air usually are independent of roughness[29]. In the experimental boiler of Leaf *et al.*,[30] smooth heating surface (of copper) gave rise to large bubbles (and a less stable foam), while on a copper surface "punched with a nail so that a lot of sharp points stick out" small bubbles originated.

The advancing contact angle θ_A being greater than θ also may be of importance in boiling. It is known that a point on a hot solid at which a bubble formed once remains for a time source of new bubbles. Presumably the main reason for this behavior is the fact (see (b) above), that the escaping bubble is smaller than the sessile

bubble and leaves behind a small gas residue which serves as nucleus for the subsequent bubble. The small residual bubble is not swept away by the liquid, even if the equilibrium contact angle is zero, presumable because θ_A is much greater than zero.

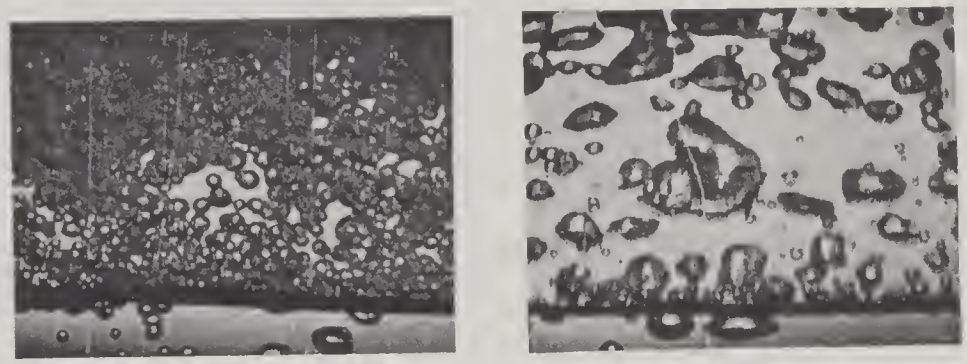
As with the bubbles formed at an orifice (see section 4), the maximum dimensions of bubbles rising from a solid plane depend on the rate of their formation. Jakob[25] found that the diameter of steam bubbles produced on a heated surface was 1, 2, 3, 4, and 5 mm when bubbles escaped every 0.014, 0.021, 0.029, 0.034, and 0.040 sec, respectively. Jenckel and Hammes[31] measured the volume of hydrogen bubbles rising from an aluminum surface during cathodic polarization in hydrochloric acid. When the rate of hydrogen evolution was raised by increasing either the concentration of the acid or the current density, the bubble volume increased also. It was, for example, 0.5×10^{-7} cm^3 in N hydrochloric acid and 16×10^{-7} cm^3 in $3N$ hydrochloric acid.

Experiments on bubble formation by electrolysis are not well suited for studying the effect of rate on the volume of the bubble, because also the composition of the solution adjacent to the electrode varies when the rate of gas evolution is altered. At the same time the potential difference between the electrode and the adjacent solution changes. Thus, bubbles produced at different rates are produced in different liquids and different electric fields. The electric state of the system can affect the size of an escaping bubble by at least two mechanisms. (a) As the interfacial tension between liquid metals and electrolyte solutions depends on the potential difference φ at the metal-solution boundary (the electrocapillary effects), and the contact angles depend on the interfacial tension, θ is affected by φ. Hence also the bubble volume is a function of φ. Kabanov and Frumkin[28] checked this conclusion. An analogous effect is observed also on solid surfaces. (b) Bubbles usually carry an electric charge (they are surrounded by an electric double layer). If this charge is of the same (opposite) sign as the charge of the electrode, the bubbles may be expected to be repelled (attracted) by the solid. A more exact treatment would require calculation of the interaction of two double layers, which calculation has not succeeded to date.

Section 12. A substance dissolved in a liquid heated by contact with a solid can influence the bubble formation in many ways. The

electric effects, just mentioned, are likely to be important when the solute is an electrolyte, but are little known. It is conceivable that the solute in a chemical reaction with, or by adsorption on, the solid will change the number of the gas nuclei present in the surface of the solid phase. However, the most common effects presumably are due to the change of γ and θ_R by the dissolved compound.

Lowering of surface tension γ tends to diminish the bubble volume. This can be inferred from Fig. 5 which shows that $v^{1/3}/a$, i.e., also (at a constant density ρ) $v^{1/3}/\gamma^{1/2}$, is a definite function of the contact angle. Thus, at $\theta = 100°$, $v^{1/3}/a$ is about 1.2, or $v^{1/3} = 1.2\ a$. If a is



A B

FIGURE 6. Effect of foam inhibitors on the bubble size in boiling liquids. (A) Boiling of dilute "Nacconol" solution; small bubbles, noncoalescing. (B) After addition of polyamide foam inhibitor; mostly large coalescing bubbles. From *Ind. Eng. Chem.*, **40**, 1363 (1948).

depressed by a solute, $v^{1/3}$ is depressed in the same ratio. In a liquid of $\gamma = 30$, the maximum bubble volume is 0.264 that in water having $\gamma = 73$ g/sec^2 (at equal densities). The reduction of v by surface-active agents can be seen, for example, in the photographs published by Gunderson and Denman[32].

Foam inhibitors added to boiling aqueous solutions (pure water requires no foam inhibitor) show, among others, the effect of increasing θ_R. This may be concluded from Fig. 6 taken from the above-mentioned paper. "A" is a photograph of a boiling dilute solution of a sodium alkyl aryl sulfonate (some very popular surface-active agents belong to this class of compounds), and "B" shows the same solution to which, however, a foam inhibitor was added. Similar photographs, but for a vertical heater, are reproduced in a paper by Jacoby and Bischmann[33].

Formation of Films

Section 13. Foams are produced by agglomeration of bubbles but they consist of films surrounding gas spaces. Therefore some methods of making foam films are mentioned here. The following discussion is based on Plateau's work[34].

Two horizontal wire rings are placed one on top of the other, wetted by a soap solution, and the upper ring is slowly lifted. Or a horizontal ring is lowered into, and then slowly withdrawn from, such a solution. As long as the distance between the two parallel rings or between the ring and the liquid surface is small, an approximately vertical film curtain suspended from the top ring is visible. When this distance increases, the film becomes strongly concave toward the exterior; finally the vertical cross section of the film acquires the shape of an X, and on further increase of the distance the upper and the lower halves of the X separate and form plane horizontal film(s) stretched across the ring(s). This development is a consequence of Laplace's law of capillary pressure (see section 10). The air surrounded by the film curtain is at the same pressure as the air outside, and gravitation may be neglected. Hence, the capillary pressure $\gamma\left(\frac{1}{R_1}+\frac{1}{R_2}\right)$ must be zero, i.e., R_1 must be equal to $-R_2$. This means that the film curtain must bulge toward the axis of revolution as its two principal radii of curvature must have different signs, i.e., must be on the different sides of the film. The distance (say, R_1) of any point of the film from the axis is equal to the radius of curvature ($-R_2$) of the film at this point in the vertical cross section. The film is a catenoid, i.e., a surface generated by rotation of a catenary about its axis. Fig. 7 shows in a qualitative way why the bulge deepens when the mutual distance between the rings increases. Let *abc* be the profile of the film when this distance is h_1. Then the distance is increased to h_2. Suppose that the new profile between *d* and *e* would still pass through point *b*. The distance R_1 for every point on the curve *dbe* is smaller than, or equal to, this distance for curve *abc*. Hence R_2 for *dbe* should also be smaller than (or in point *b* equal to) R_2 for *abc*. It is seen, however, that curve *dbe* is flatter than curve *abc*, i.e., has larger radii of curvature. Thus, *dbe* cannot represent an equilibrium figure, and the film between *d* and *e* will pass through a point, such as *f*, nearer to the axis of

revolution than b. Finally, the smallest R_1 of the curtain becomes so small that the film coalesces in the middle. According to Plateau's calculation this happens when the distance h between the rings is two-thirds of the ring diameter. For two 7-cm rings the experiment gave $h = 4.6$ cm, i.e., sufficiently close to 14/3 cm. When a ring is raised above a liquid surface, distance h should be equal to one-third of the diameter. An experiment gave $h = 2.26$ cm for a 6.96-cm ring.

An analogous sequence of events takes place when a soap bubble formed at the bowl of a pipe is thrown off by a jerk of the pipe. The rim of the bowl has the function of one of the rings in the previous

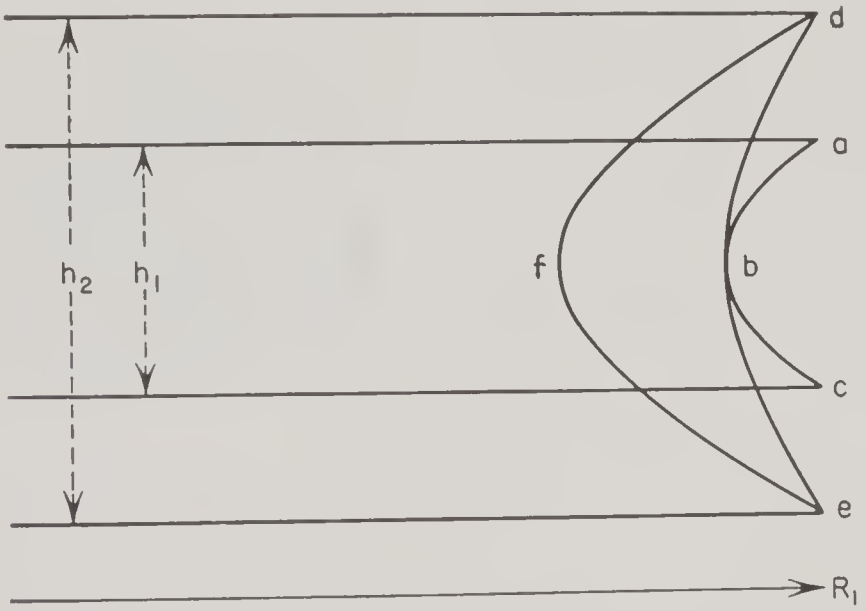


FIGURE 7. Indentation of a foam film between two rings when the distance between the rings increases.

experiment, the incomplete film sphere over the bowl acts as the other ring, and the jerk of the pipe causes the necessary increase of the distance between the "rings." Thus the bottom part of the fully formed spherical soap bubble originates from the upper half of the neck produced when the bowl was moved away from the bubble. When a ring spanned by a soap film is rapidly moved in the direction of the normal to the film, the resistance of the air transforms the plane into a bag, and the bag becomes a detached bubble in the same manner as a bubble blown from a pipe.

FORMATION OF FOAM

Section 14. When a bubble rising in liquid comes near the surface of the latter, a liquid dome is lifted above the bubble. In a liquid

incapable of foaming this dome bursts at once, producing fine spray (as in soda water). In the other liquids the dome persists for a time. During its existence it is subjected to gravitation and to capillary pressure, and these agents determine its shape and position. Plateau's *Recherches*, 6th series[34], contain practically everything we know about this problem.

When the bubble is small, it is almost spherical and almost completely submerged. There are three liquid-gas interfaces and, hence, three capillary pressures to consider. The pressure downward of the ceiling of the bubble is nearly cancelled by the pressure upward of the floor of the bubble, as the curvatures of ceiling and floor are nearly equal. The pressure downward of the roof of the bubble, i.e., of the curved free surface of the liquid above the bubble, is cancelled by the bubble's buoyancy. As the bubble is small, the buoyancy also is small, and consequently the radius of the curvature of the exterior of the dome is large. Plateau did not determine the relation between the radius (R) of the bubble and the radius of curvature (R^1) of the dome, but an (unpublished) calculation shows that, at a first approximation for very small R,

$$R^1 = \frac{3\gamma}{2\rho g R}, \tag{6}$$

γ and ρ being again surface tension and density of the liquid, and g acceleration due to gravity. For water at room temperature, when $R = 0.1$ cm, R^1 is 0.6 cm (using a more exact formula).

When the bubble diameter is over 2 cm, the floor of the bubble is nearly plane and the dome is nearly a hemisphere. An equation attributed to Mensbrugghe shows this in a semiquantitative manner. In a large bubble the exterior and the interior surfaces of the dome are almost parallel. Let the angle formed by them and the imaginary horizontal plane which separates ceiling and floor be α, and the angle formed by the floor with this plane be β. Then the surface tension γ of the plane liquid surface outside the bubble is equilibrated by the tension $\gamma(2 \cos \alpha + \cos \beta)$ of the three bubble surfaces. Hence, $2 \cos \alpha + \cos \beta = 1$. Thus a flat floor ($\beta$ very small) implies a very small $\cos \alpha$, i.e., α of approximately 90°, i.e., a nearly hemispherical shape of the dome.

The exterior surface of the dome *gradually* merges with the plane surface of the liquid far from the bubble. In fact, the shape of the roof is identical with that of liquid perfectly wetting a glass marble having the shape and position of the bubble.

If there are two bubbles underneath the liquid surface and their mutual distance is so small that the surface between them is curved everywhere, then the bubbles are attracted to each other in the same manner as are two parallel vertical plates partly immersed in a liquid (see, e.g., ref 1, p. 31). If many such bubbles come together, the first layer of a foam column is formed.

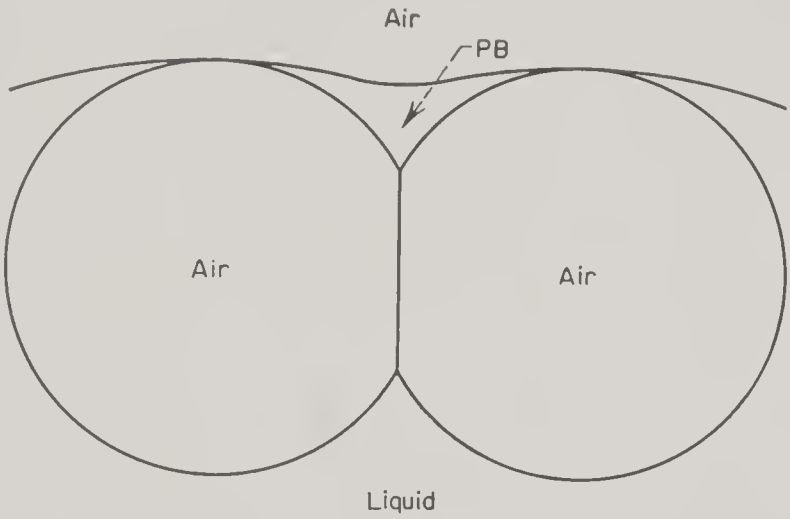


FIGURE 8. Mutual deformation of two foam bubbles in contact in the top layer of foam.

STRUCTURE OF FOAM

Section 15. When two bubbles come together on a liquid surface, they—as a rule—both suffer deformation, as illustrated in Fig. 8. The septum between the bubbles has a curvature (radius R^1) different from those of the bubbles (radii R_1 and R_2). R^1 is given by the condition that the resultant pressure on the septum should be zero. In the bubble having radius R_1 the capillary pressure is $4\gamma/R_1$. The factor is 4 rather than 2 because the lamella has two surfaces each of which has surface tension. In the other bubble it is $4\gamma/R_2$. The capillary pressure exerted by the septum is the difference between these pressures, i.e., $4\gamma/R^1 = (4\gamma/R_1) - (4\gamma/R_2)$. Hence,[35]

$$R^1 = \frac{R_1 R_2}{R_2 - R_1} \tag{7}$$

If the two bubbles are equal, $R_2 = R_1$ and $R^1 = \infty$, i.e., the septum is plane, as in Fig. 8. If $R_2 \gg R_1$, R^1 is not greatly different from R_1. This means that in the region of contact the very large bubble is

more deformed than the small one. If $R_2 = 2R_1$, then $R^1 = R_2$, i.e., the larger bubble is not deformed at all.

The space marked PB plays an essential part in Plateau's theory of foam. The liquid in this space is under a lower pressure than the liquid in the walls of the bubbles. Let the pressure in the bubble be P. The pressure in the liquid in the wall (gravitation being neglected) is $P_1 = P - \frac{2\gamma}{R_1}$ if R_1 is the common value of the two main radii of curvature of the interface between gas phase and bubble wall. The pressure in space PB is $P_2 = P - \gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$, if R_2 is that radius of curvature of the interface between PB and the gas phase, which lies in the plane of paper (see Fig. 9). Thus $P_1 - P_2 = \gamma\left(\frac{1}{R_2} - \frac{1}{R_1}\right)$, and as R_2 is much less than R_1, P_1 is greater than P_2. The importance of this pressure difference for foam drainage is discussed in section 56. Here the influence of PB on foam structure is presented. PB means *Plateau's border*. This term will be used henceforth in this book. Sometimes Plateau's border is designated Gibbs edge or Gibbs ring, but Plateau[36] anticipated Gibbs by almost 30 years and his work was known to Gibbs.

In the presence of a free liquid surface the shape of Plateau's border may be markedly affected by gravitation. In a system of bubbles, whose thin walls follow capillary pressures rather than gravitation forces, this shape can be determined from capillary considerations alone. The main conclusion of such considerations is that the three lamellae radiating from a Plateau border make angles of 120° with each other. This can be shown by using the notion of either surface tension or capillary pressure (see Fig. 9). (a) The surface tension of the three lamellae (or rather of their six surfaces) is the same. Hence the border is subjected to the action of three (or rather three pairs of) equal forces (2γ) in one plane. These can cancel each other only if inclined to each other at 120°. (b) Of the two principal radii of curvature of one of the surfaces of the border (e.g., that in contact with the lower bubble of Fig. 9) one—normal to the plane of the drawing—is not very different from the radius of the bubble, while the other, in the plane of the drawing, is very small. The expression $\gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$ for the capillary pressure on Plateau's border, if $R_1 \gg$

R_2, can be approximately simplified to γ/R_2. Thus the capillary pressure on Plateau's border is almost independent of the size of the bubble. Hence, whatever the size (and the relative size) of the three bubbles, the curvatures of the border in the plane of the paper must be identical for its three surfaces. This is possible only if the angles between the lamellae are equal, that is, each is equal to 120°.

If instead of three, four lamellae should come together, they would form a perfect cross, i.e., the angles between them would be 90° each.

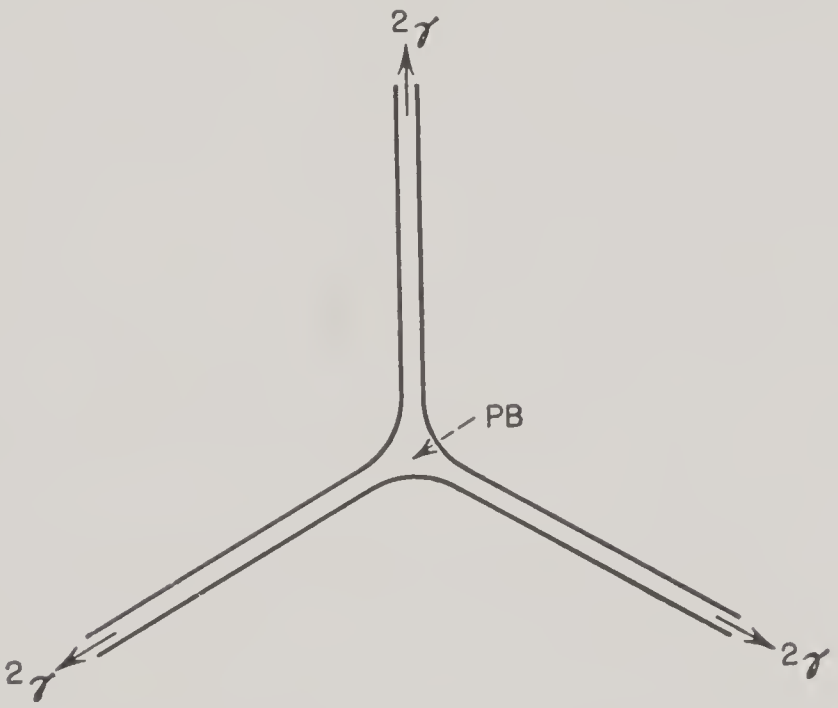


FIGURE 9. Three foam lamellae coming together in a Plateau border and forming angles of 120° with each other.

However this structure would be unstable. Only by a rare coincidence would the pressures in all the four bubbles be equal. Suppose the pressure in the S.W. bubble is greater than in the S.E. bubble. The pressure excess would shift the septum to the east and, instead of one crossing of four lamellae, there will emerge two joints of three lamellae each. If only three bubbles meet, pressure differences will shift the septums but will not alter the number of bubbles adjacent to one Plateau's border. As a rule, therefore, in every foam structure three and only three lamellae radiate from every line of contact[37].

Four such lines of contact may come together to one point. Then they form with each other angles of 109° identical with those between the four valencies of a carbon atom or between the lines connecting

the center of a regular tetrahedron with its four corners. Four bubbles arrange themselves into a tetrahedron-like structure because tetrahedron is the only close tri-dimensional figure having four corners. Figures having more, e.g., eight corners as in a cube, in which more than four lines of contact come together, are unstable, and the cause of this instability is identical with that for the instability of more than three bubbles touching each other in one plane. The tetrahedron-like structure is based on the *regular* tetrahedron because (a) surface tension is identical for all the Plateau borders, or, from another point of view, (b) because capillary pressure must be the same on different surfaces of a border.

Plateau did not deduce the crystal shape approximating the most probable shape of a bubble in foam. From observations on gelatin, soap, and rosin foams Desch[38] concluded that pentagonal dodecahedron (figure bounded by twelve equilateral pentagons) is the most frequent approximate shape of foam bubbles. This is the only figure whose repetition can fill the space and in which all faces form angles of 120° with each other.

References

1. Bikerman, J. J., "Surface Chemistry for Industrial Researeh," New York, Academic Press, 1947.
2. Maier, C. G., *U. S. Bur. Mines Bull.*, **260**, (1927).
3. Kovalski, W. v., and Wacker, A., *Ber.*, **63**, 1698 (1930).
4. Guyer, A., and Peterhans, E., *Helv. Chim. Acta*, **26**, 1099 (1943).
5. van Krevelen, D. W., and Hoftijzer, P. J., *Chem. Eng. Progress*, **46**, 29 (1950).

5a. Datta, R. L., Napier, D. H., and Newitt, D. M., *Trans. Inst. Chem. Engrs (London)*, **28**, 14 (1950).

6. Remy, H., and Seemann, W., *Kolloid-Z.*, **72**, 279 (1935).

6a. Coppock, P. D., and Meiklejohn, G. T., *Trans. Inst. Chem. Engrs (London)*, **29**, 75 (1951).

7. Remy, H., and Seemann, W., *Kolloid-Z.*, **72**, 3 (1935).
8. Eversole, W. G., Wagner, G. H., and Stackhouse, E., *Ind. Eng. Chem.*, **33**, 1459 (1941).

8a. Pattle, R. E., *Trans. Inst. Chem. Engrs (London)*, **28**, 32 (1950).

9. Schnurmann, R., *Kolloid-Z.*, **80**, 148 (1937).
10. Savitskaya, E. M., *Kolloid. Zhur.*, **13**, 309 (1951).
11. Am. Soc. Testing Materials Book of Standards 1946, III A, p. 853, Method D 892 – 46 T.
12. Bragg, L., and Nye, J. F., *Proc. Roy. Soc. (London)*, **190A**, 474 (1947).
13. Smith, C. S., *J. Applied Phys.*, **20**, 631 (1949).

13a. Achorn, G. B., and Schwab, J. L., *Science*, **107**, 377 (1948).

14. Gilberg, D., and Anderson, R. A., *J. Applied Phys.*, **19**, 127 (1948).
15. Melsens, *Compt. rend.*, **20**, 1658 (1845).

16. Plateau, J., *Mém. acad. roy. sci. Belgique*, **37** (1869). 11th ser.
16a. Fry, J. F., and French, R. J., *J. Appl. Chem.*, **1**, 425, 429 (1951).
17. Dean, R. B., *J. Applied Phys.*, **15**, 446 (1944).
18. Harvey, E. N., McElroy, W. D., and Whiteley, A. H. *J. Applied Phys.*, **18**, 162 (1947).
19. Harvey, E. N., Cooper, K. W., and Whiteley, A. H., *J. Am. Chem. Soc.*, **68**, 2119 (1946).
20. Bateman, J. B., and Lang, J., *Can. J. Research*, **23E**, 22 (1945).
21. Krause, A., and Kapitańczyk, K., *Kolloid-Z.*, **80**, 273 (1937).
22. Kapitańczyk, K., *Chem. Abs.*, **44**, 7119 (1950).
23. Gernez, D., *Ann. chim. phys.* [5], **4**, 335 (1875).
24. Larson, R. F., *Ind. Eng. Chem.*, **37**, 1004 (1945).
25. Jakob, M., *Mech. Eng.*, **58**, 643 (1936); see also Gunther, F. C., *Trans. Am. Soc. Mech. Engrs.*, **73**, 115 (1951).
26. Bashforth, F., and Adams, J. C., "An Attempt to Test the Theories of Capillary Action," Cambridge, 1883.
27. Wark, I. W., *J. Phys. Chem.*, **37**, 623 (1933).
28. Kabanov, B., and Frumkin, A., *Z. physik. Chem.*, **A165**, 433 (1933); **A166**, 316 (1933).
29. Bikerman, J. J., *J. Phys. & Colloid Chem.*, **54**, 653 (1950); *J. Colloid Sci.* **5**, 349 (1950).
30. Leaf, W. B., *et al.*, *Am. Ry. Eng. Assoc.*, **45**, *Bull.* **441**, 58 (1943).
31. Jenckel, E., and Hammes, H., *Z. anorg. allgem. Chem.*, **233**, 415 (1937).
32. Gunderson, L. O., and Denman, W. L., *Ind. Eng. Chem.*, **40**, 1363 (1948).
33. Jacoby, A. L., and Bischmann, L. C., *Ind. Eng. Chem.*, **40**, 1360 (1948).
34. Plateau, J., *Mém. acad. roy. sci. Belgique*, **33** (1861) 5th and 6th ser.; **36** (1867) 7th ser.
35. Plateau, J., *Mém. acad. roy. sci. Belgique*, **33** (1861) 6th ser.
36. Plateau, J., *Mém. acad. roy. sci. Belgique*, **23** (1849) 2nd ser.
37. Plateau, J., *Mém. acad. roy. sci. Belgique*, **33** (1861) 5th ser.
38. Desch, C. H., *Rec. trav. chim.*, **42**, 882 (1923).

2. METHODS OF MEASURING FOAMINESS

Section 16. In sections 14 and 15, foam bubbles and their agglomerations have been considered as equilibrium systems. In reality, however, hardly any foam is in equilibrium. Two main processes take part in the large majority of foams. The liquid making out the domes of single bubbles or the walls in a multicellular foam drains down because of gravitation and toward Plateau's borders because of the suction they exert. This drainage is the subject of Chapter 4. The other process consists in bursting of the foam films, and the present chapter reviews the main methods suggested for measuring the lifetime or *persistence* of these films.

The final goal of all such methods should be establishing foaminess as a quantity independent of the apparatus and procedure employed and depending only on the nature of the substances used, their mixing ratio, and on the general physical factors (such as temperature, pressure, etc.) Surface tension, density, etc., are quantities in this sense. The ideal is to be able to express the foaming capacity or the foam persistence of a liquid by one number. This ideal has not been reached yet, and even the desirability of reaching it seems to be felt by a minority of the students of foam.

Section 17. The persistence of *single films* spanning a wire ring may depend on the material of the ring. Plateau[1] could not obtain persistent soap films on loops of untreated iron wire and had to oxidize the wire by immersing it for a minute in dilute nitric acid. Perhaps, nitric acid increased the roughness of the iron surface and, hence, retarded its de-wetting. Foulk and Barkley[2] noticed no difference in behavior between platinum, chromel, and glass rings. Film formation is more probable if the ring is exactly parallel to the liquid surface from which it is being withdrawn and if the rate of withdrawal has a definite value[2]. The apparatus constructed by Foulk and Barkley is shown in Fig. 10. K is the ring (0.05 cm platinum wire,

diameter 1.3 cm). When it is pressed down to touch the liquid overflowing in funnel G and then released, the rubber spring V lifts it at a reproducible speed. The liquid was distilled into funnel G from flask A, and the overflow siphoned away through tube I. (For explanation

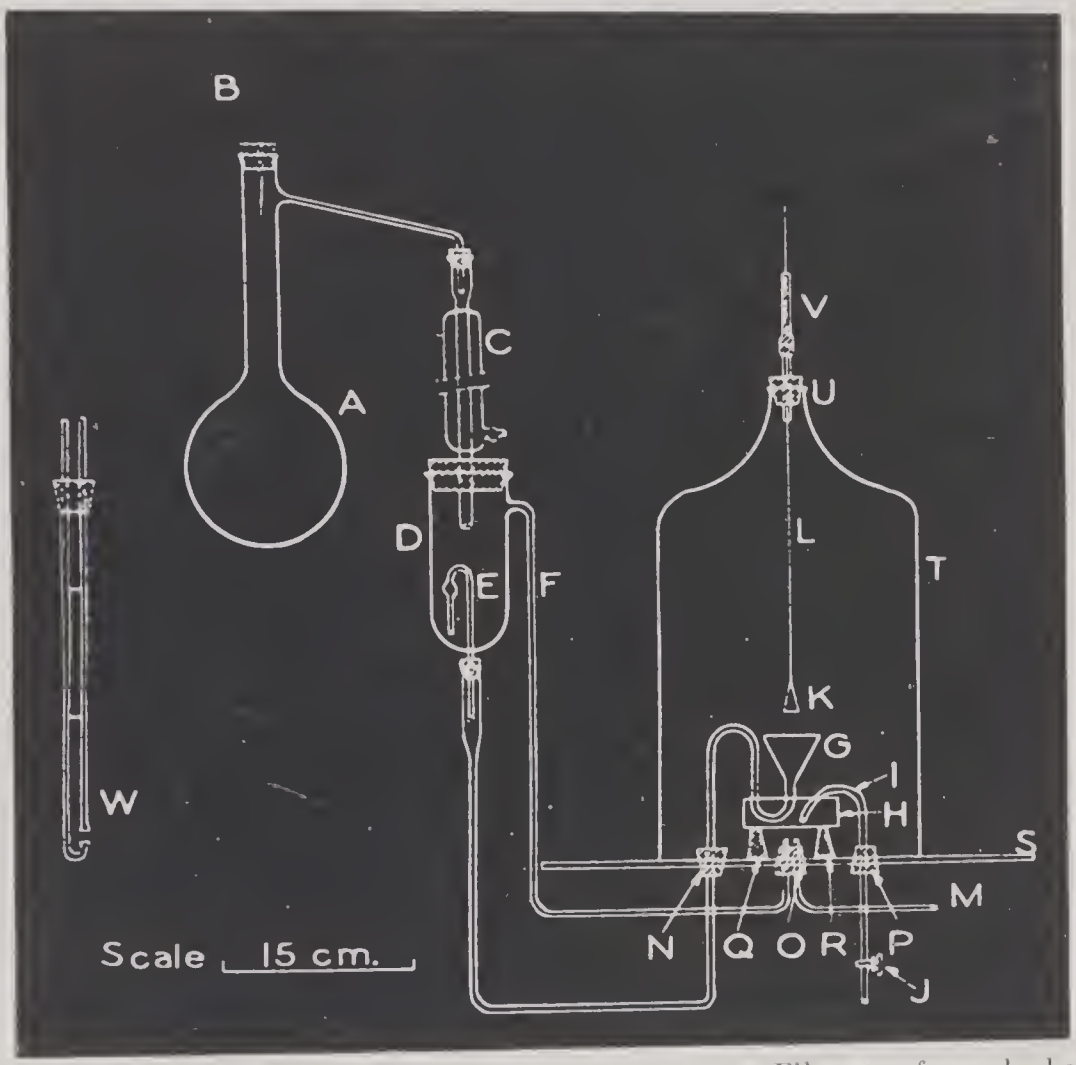


FIGURE 10. Apparatus for measuring film persistence. Films are formed when ring K touches liquid in funnel G and is lifted again. From *Ind. Eng. Chem.*, 35, 1013 (1943).

of W see section 19.) Foulk and Barkley tested the foaming capacity of their liquids by immersing and withdrawing the ring 100 times and noting the number of films formed. Plateau, whose soap solutions invariably gave films, measured the persistence of the latter.

Plateau[3] prepared soap films also by rolling soap solutions in a cylindrical tube and suddenly stopping the movement. Because the curvature of Plateau's borders on both sides of the film must be identical, the films are normal to the walls of the tube. Hence, if the

tube is conical, they are convex toward the wider part of the tube and may be pushed in this direction by capillary pressure. Mild shaking of a foaming solution in a graduated flask readily gives rise to such films. Films in a cylinder can be produced also by blowing air through a fine pipette on the surface of an appropriate liquid in a cylindrical vessel[4].

An apparatus for the determination of the persistence of vertical

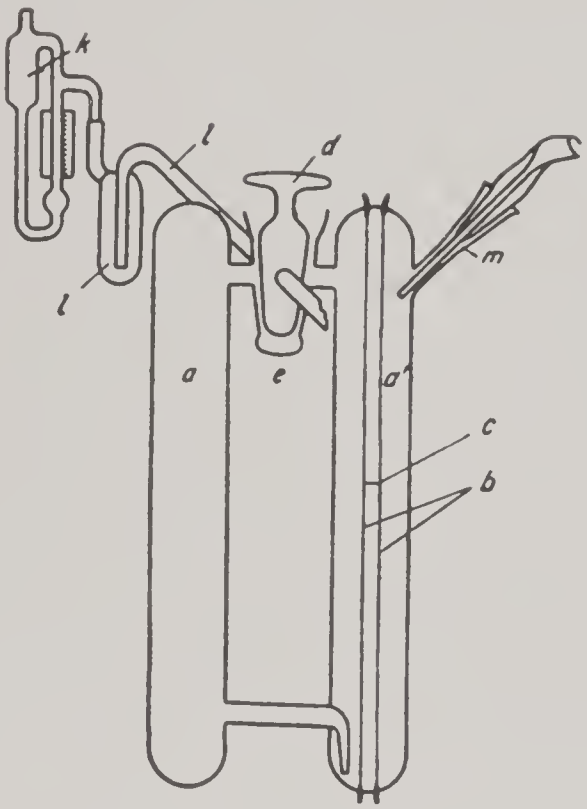


FIGURE 11. Apparatus for measuring the persistence of vertical foam films in a controlled atmosphere. The films are spanned between the parallel wires b and the cross-wire c. From *Compt. rend. acad. sci. U.R.S.S.*, **52**, 317 (1946).

films in a closed vessel[5] is shown in Fig. 11. Two parallel platinum wires (*b*) are sealed in a glass tube (a^1) and connected with each other by the short wire (*c*). The solution is introduced through *m* so that its level is above *c*. Then it is gradually pressed into container *a*, and the gas escapes through stopcock *d*, trap *l*, and rheometer *k*. When the surface of the solution descends below *c*, a film stretched between *c* and the two wires *b* remains. Its persistence can be measured.

Stokes[6] determined the lifetime of growing bubbles. The bubble formed from a drop of liquid was increased at a constant rate by injection of air, and the time of its bursting was noted. If the amount

of liquid transferred into the bubble wall was known, the film thickness in the moment of rupture could be calculated.

When a vertical wire triangle is slowly withdrawn from a solution, a film remains between the exposed parts of two wires. The area of the film in the moment of rupture is greater the greater the foaming capacity of the liquid and may be used to measure this capacity[7]. Matalon[8] determined the force exerted by the liquid film on a vertical stirrup alternately lowered into liquid and raised above it; the hysteresis observed is said to have some connection with foaminess.

Section 18. Single films are particularly favorable subjects for studying the relation between persistence and *extent* and the effect of the *surroundings* on persistence.

As a rule, the lifetime of a film is greater the smaller the film area. In Plateau's experiments[9] soap films on an iron ring, diameter 7 cm, lasted an hour at the most, while films in a 2-cm ring reached persistence of 12 hours (no mean values are given). It is seen that the maximum persistencies were (roughly) inversely proportional to the area of the film [as $(7/2)^2 = 12.2$]. An identical relation was observed also for the mean values of lifetime[4]. Films 1.0 cm in diameter were compared with those having diameter of 3.5 cm, the ratio of the areas being again 12.2. The persistence of the smaller films of 0.43 per cent disodium α-tocopheryl phosphate monohydrate solution, 3.7 per cent sodium laurate solution, and of (7 weeks old) beer were approximately 420, 260, and 390 sec, while those of the larger films of the same solutions were 35, 23, and 35 sec, respectively. The ratios (14.0, 11.3, and 11.1) are not far from 12.2. The lifetime of some bubbles (see section 19) also is inversely proportional to the square of their radius. The persistence of vertical films (of aqueous alcohols) produced in the apparatus of Fig. 11 was smaller the greater the film area, but no quantitative results are mentioned in the original. If the relation $\frac{\tau_1}{\tau_2} = \frac{S_2}{S_1}$ (τ = persistence, S = area) is valid for many solutions, the quantity $\tau_1 S_1 = \tau_2 S_2$, which would be independent of the area, would be a better measure of foaminess than τ_1 or τ_2. Use of τS would be a step toward the goal mentioned in section 16. For Plateau's explanation of the inverse relationship between persistence and area see section 75.

The lifetime of a film depends on whether the film is kept in an

open or a closed vessel and whether the atmosphere is humid or dry. The atmosphere in a closed vessel (containing at least one liquid film) will usually be more humid than that in an open vessel; thus the two sets of conditions are related. However, it is certain that the environment of a film in a confined space differs from that in a large room not only because of different humidities. In a closed vessel the film is better protected from external foes such as strong air currents, dust particles etc., and is likely to persist for a longer time (see section 102). If it is inherently more persistent in dry air, then the higher humidity in the closed vessel will counteract the beneficial effect of the mechanical protection, and the lifetime may be either shorter or longer.

Plateau[3] studied films (or rather bubbles on a wire frame) of soap solutions in aqueous glycerol (see section 39). These films were hygroscopic and increased in thickness when kept in moist air. They persisted for a longer time in a vessel over calcium chloride. Vertical films of aqueous alcohols on wire triangles[7] ruptured at a greater extension in an open than in a closed vessel, but no such effect was observed with water or alcohol alone. Plane films in closed tubes were particularly persistent[3]. For example, films of soap in aqueous glycerol lasted for 10 days as against 6 hours for a comparable bubble on a wire ring in air. Also, the films which Dewar[10] succeeded in preserving for months were plane, horizontal, and kept in a closed bottle.

Plateau[3] pointed out the importance of vibrations (of the film or of the whole apparatus) but made no systematic experiments concerning it.

The effect of the environment is mentioned again below (section 19). It is necessary to emphasize its significance in this discussion of the methods of measuring foaminess, as neglect of this effect may vitiate any comparison of the experimental results obtained under different conditions or at different times.

Section 19. The lifetime of *bubbles* underneath a liquid surface (see section 14) also is greater the smaller the bubble. This was noticed by Plateau who, however, did not study the problem in a quantitative manner. In later experiments it was found that the persistence was (roughly) inversely proportional to the diameter $2R$ of the bubble or to the square of this diameter. Thus[11], in $0.005M$ sodium oleate solution the lifetime was 23 min. for bubbles of 0.1

cm and 4.5 min. for bubbles of 0.4 to 0.5 cm; this is proportionality between $\frac{1}{\tau}$ and $2R$ (see also section 30). The lifetime of mercury bubbles (see section 7) was inversely proportional to R^2 (see ref. 12).

The persistence greatly depends on the cleanness of the surface. Liquid surfaces are cleaned by overflow or, more often, by sweeping them with a bar of a nonwettable solid[11, 13]; this method is familiar to all students of unimolecular layers. Sometimes[11] it is found necessary to wait one or two minutes before placing a new bubble on (or under) the spot where the previous bubble burst or to place every new bubble under a virgin surface. Also, the age of the surface undisturbed by bubbles has an effect on persistence. The difference between a fresh (continuously overflowing) and an aged (about 20 min. old) surface is well illustrated in the observations by E. E. Wark[14]. The lifetime of bubbles of 0.002 per cent trimethylcetylammonium bromide was 2 sec under fresh and 19 sec under aged surface, and the corresponding values for 0.02 per cent terpineol solution were 12 and 22 sec.

As in the instance of single films (section 18) the results in an open and a closed vessel often are strikingly different. Thus the persistence of air bubbles in aqueous alcohol showed a maximum at some medium alcohol concentration (see section 34) when the vessel was closed, but no such maximum was observed in free air. The persistence of bubbles in $0.4N$ aluminum chloride solution was doubled when an open trough was substituted for a closed vessel[15]. Bubbles in 0.00092 and $0.0184M$ isoamyl alcohol solutions lasted in free air 5 to 10 times as long as in enclosed space[11] (see also section 45).

An apparatus using *two bubbles* was devised by Foulk and Miller[16]. A simplified version[2] is shown in Fig. 10, *W*. It consists of two vertical capillary tubes, one of which is bent so that its orifice is exactly under the orifice of the other tube. The instrument is partly immersed in the test liquid, deep enough for the orifices to be submerged. When air is forced through both tubes, bubbles form at both orifices. In a liquid incapable of foaming they readily coalesce. Otherwise they rise separately without merging. The percentage of bubbles which rose separately is taken as a measure of foaminess. It depends on the distance between the orifices[17], the precision of alignment of the two bubbles, etc., and thus does not determine foaming capacity in a generally valid manner. On the other hand, the method has the advantage of employing fresh gas/liquid interfaces produced in the

bulk of the liquid and should be less sensitive to surface contamination than the one-bubble method[2]. The two-bubble principle was adopted also by McBain and Robinson[18].

In another method[19] many bubbles are produced but only one is utilized. The surface of a liquid is covered with one layer of bubbles (blown at the tip of a submerged capillary). Then a wire ring enclosing an area S equal to one-half the surface area of the liquid is fixed above the liquid, and the time required for area S to become free of foam is noted. In other words, the lifetime of the most persistent bubble among an indefinite number of these is determined while all the other bubbles are disregarded. The effect of surroundings is noticeable in this method also. In 0.01 per cent saponin solution the maximum lifetime was found to be too long for convenient measurement if the monolayer of bubbles was formed in a closed vessel or protected from draft by a 40 cm tall wall; but when the wall was 2.5 cm tall the lifetime was several seconds only. Increase of the bubble path in the liquid (i.e., the distance between the orifice and the surface of the liquid) from 6 to 76 cm extended the lifetime from 6.5 to 15.5 sec.

Section 20. Three-dimensional foams, i.e., those containing at least two bubbles in every direction, are commonly used for determining the foaminess of a liquid. The three main methods for producing such foams are bubbling, also called pneumatic method (see sections 3–6); agitation (see section 7); and boiling (see sections 9–12). For experiments of fundamental nature bubbling is more advantageous than the other procedures since the amount of gas introduced into the liquid and the degree of its dispersion can be regulated at will and determined with relative ease. Several students of foams produced by whipping, beating, etc., emphasized the difference between the ease of formation of froth and its stability. This means that standard agitation of liquid A may give rise to less foam than that of liquid B, but the froth of B, once produced, may be more persistent than that of A. In this instance it was more difficult to introduce bubbles into A than into B. In the bubbling method the gas is introduced at a predetermined rate and a predetermined pressure, from measurable orifices, etc., and the ease of formation cannot readily be distinguished from the stability of a froth (see also sections 26 and 48).

Section 21. In the *pneumatic* method, bubbles may originate at single orifices[20], in a cloth filter[21], in sintered glass filters[22, 23, 24], in a diffuser stone[25], in a Pasteur-Chamberland filter, in a diffuser of sintered metal powder, or in any other suitable porous septum. Only when a single orifice is employed, may the resulting foam be expected to consist of equally large bubbles.

Figs. 12 and 13 represent two of the apparatuses used in the pneumatic method. That[22] of Fig. 12 has no provision for easily keeping

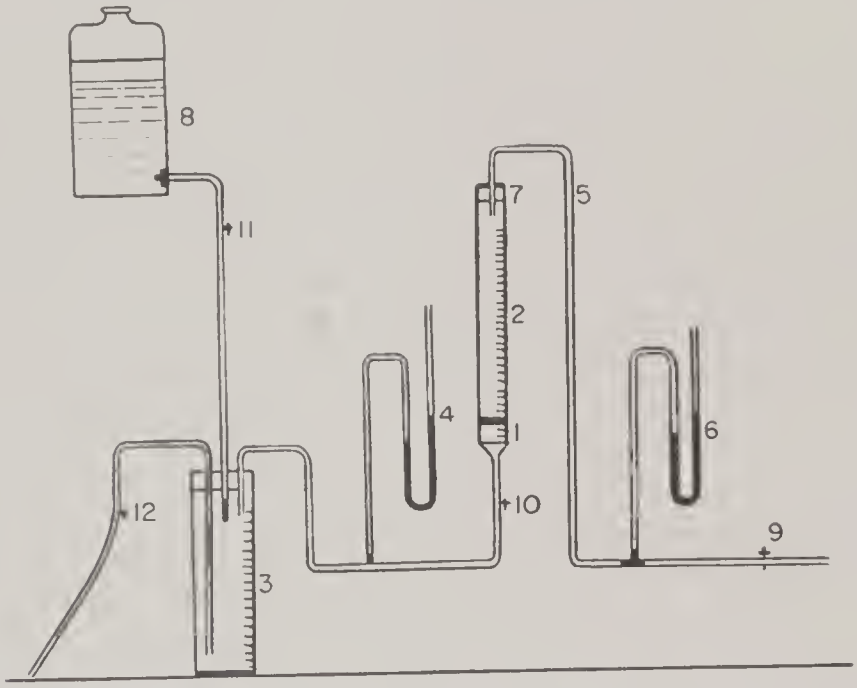


FIGURE 12. An apparatus for the pneumatic determination of foam stability. 1, sintered glass filter; 2, measuring tube; 3, graduated cylinder; 4, manometer; 5, outlet tube; 6, manometer; 7, stopper; 8, aspirator with water; 9, 10, 11, and 12 are stopcocks. From *Tsvetnye Metally*, **6**, 1546 (1931).

the pressure of the ingoing gas constant but allows measuring the pressure of the outgoing gas and the increase of pressure in the measuring cylinder (tube 2) occurring because of the bursting of the bubbles (see section 56). In the instrument[24] of Fig. 13, gas is forced into the solution under a constant pressure but after traversing the "one-meter" measuring tube it simply goes to waste. This instrument is convenient if several different gases are to be used.

Many quantities can be measured with any of these or similar instruments. Of the two most important, the rate of collapse of preformed foam is discussed in section 28, while the foam height (from which bubble persistence is calculated) is reviewed in the two fol-

lowing sections. The measurement of the foam height *during* the bubbling is often referred to as the *dynamic method* of determining foaminess. It is this dynamic foam height which is treated in section 22.

Section 22. *Foam height* is the difference in level between the top and the bottom of the foam column in a graduated tube. When the

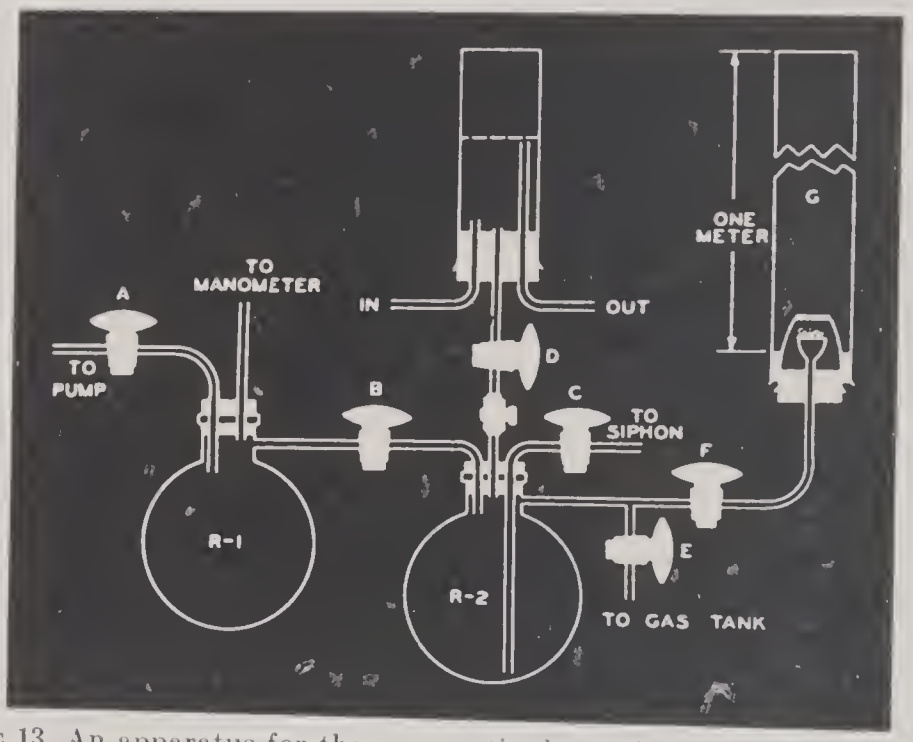


FIGURE 13. An apparatus for the pneumatic determination of foam stability. G, measuring tube; A, B, C, D, E, and F are stopcocks. From *Ind. Eng. Chem.*, **32**, 1594 (1940).

froth persistence is small, the froth usually consists of small bubbles the upper boundary of which scarcely moves up or down the tube as long as the rate of the air current is constant, and the position of this boundary is easily read up. In strongly frothing solutions the top boundary may consist of films spanning the whole tube and rising with the velocity of the air current; in this instance, the level at which every single film has burst is noted, and then the arithmetic mean is taken. If the bottom of the froth column is sharp, it is read directly. Otherwise it is usually permissible to identify the lower boundary of the froth with the upper boundary of the liquid as it existed before frothing.

The foam height h in the steady state depends on the rate of gas current. Within a range, h is proportional to the linear gas velocity u. For instance, the ratio h/u was 4.7, 6.5, 6.8, 6.8, and 6.4 sec for u equal to 0.130, 0.247, 0.395, 0.498, and 0.669 cm/sec, respectively, all for 1 per cent solution of butyl alcohol[23].

In Sasaki's experiments[26] on an aqueous solution of 1-hexanol, the foam height was a linear function of u but not proportional to it, and the ratio $(h - a)/u$ rather than h/u was stated to be constant, a being a correction term. This statement implies that the foam height is equal to a cm when $u = 0$, i.e., no gas is injected at all; thus it cannot be true at small u. At great u, a was much smaller than h and could be neglected. Unfortunately it is not clear what range of air rates was explored by Sasaki. Dyakonov[27] determined h/u as function of the Reynolds number (Re) defined as $\rho ud/\eta$, ρ being the density of the liquid, η its viscosity, and d the diameter of the measuring tube. In dilute soap solutions, h/u was constant as long as Re was less than 100, or, as d was 4 cm, as long as u was less than about 0.25 cm/sec. Between Re = 100 and Re = 200 or 250, h/u increased with u. At still greater Re it decreased again, presumably because the air blast ruptured the soap lamellae. In 0.1 per cent isobutyl alcohol solution[28], h/u remained constant (about 3.2 sec) up to $u = 1.3$ cm/sec and increased at greater u, the highest value of u tested being 2 cm/sec.

If S is the cross section of the measuring tube, the foam volume $v = Sh$, and the veolocity $u = V/St$, V being the gas volume forced through the porous membrane during time t. Hence, v is proportional to V/t (within a range). This form of the rule is preferable if the cross section of the tube is not constant[23]. If foam columns in two different tubes are compared at a constant value of V/t, the foam *volumes* should be equal. This was confirmed for tubes of 2.7 and 3.7 cm in diameter and also for a tube fitted with a bulb. Urine and 1 per cent butyl alcohol were the liquids used[23]. Another confirmation seems to be afforded by foaming of raw sugar solutions[20]. When the cylinder diameter d was varied between 2.5 and 4 cm, the foam height h varied according to a relation expressed by the authors as $(h_1/h_2) = (4.7 - d_1)/(4.7 - d_2)$. This equation cannot be correct as it yields $h_1 = 0$ at $d_1 = 4.7$ cm. However, from it the foam heights at 2.5 and 4 cm are calculated to be in the ratio 3.14, i.e., the foam volumes in the ratio 1.23 : 1. In these experiments V/t was 17 cm^3/sec.

When the height H_0 of the liquid layer above the porous septum

(before bubbling) increases, the foam height also increases but seems to tend to a constant limit[23]. For instance, vt/V of 1 per cent butyl alcohol was 4.0, 5.6, 6.7, and 7.1 sec when H_0 was approximately 0.5, 1.0, 1.5, and 2.0 cm. In Dyakonov's experiments h/u was said to be proportional to $H_0^{0.8}$.

As long as the conditions are such that v is proportional to V/t and that the ratio vt/V increases to a constant limit when H_0 increases, this limit

$$\Sigma = \frac{vt}{V} \tag{8}$$

is independent of the rate of air flow, of the diameter of the measuring tube, and of the amount of the liquid used. Thus the quantity Σ seems useful for characterizing the foaming capacity of a liquid (see section 16). Σ proved to be independent also of the porosity of the septum[23] (sintered glass filters), but this observation does not imply that Σ is independent of the bubble diameter as this varies but little with the pore size when the pores are near each other (see section 5).

Σ has the dimension of time. It is equal to the time an average bubble remains entrapped in the foam[23]. This can be shown as follows. Let n be the number of bubbles formed in unit time. Then, in the steady state, the total number of bubbles in the foam column is $n\Sigma$, as we assume that all bubbles older than Σ sec burst and give their air content to the outside. If the mean volume of a single bubble is v_0, the volume of air transformed into foam in the unit time is nv_0, and the foam volume is $nv_0\Sigma$. But $nv_0 = V/t$ and $nv_0\Sigma = v$, thus giving equation (8). This derivation disregards rupture of film which does not result in liberation of air and also the volume of the liquid in the foam.

Section 23. When the Σ of a solution is so large that unwieldy foam volumes would be obtained by continuing the experiment until the steady state is reached, an estimation of the foaminess is achieved by comparing the rate of rise of foam with the rate of injection of gas. If foam lamellae are infinitely stable, the rate dv/dt of the increase of the foam volume is equal to that, dV/dt, of the air flow. If the average persistence of a bubble is Σ sec, the equation

$$\frac{dv}{dt} = \frac{dV}{dt} - \frac{v}{\Sigma} \tag{9}$$

seems to be a promising approximation. In steady state, $dv/dt = 0$, and equation (9) is reduced to equation (8) as $dV/dt = V/t$ as long as the air current has constant velocity. It is clear from equation (9) that, as long as persistence Σ is great, dV/dt is practically equal to dv/dt independently of the exact value of Σ. Thus, the rate dv/dt cannot be used as a measure of foaminess if Σ is too long. The use of dv/dt for determination of foaminess in these instances has been criticized long ago (see, e.g., ref. 29) but is not yet quite abandoned (see ref. 30).

Instead of equation (9) Aleĭnikov[22] used the following formula for U_d, the "average rate of dynamic coagulation": $U_d = (V - v)/t$. If of the air volume V introduced, only the volume v remained in the foam, then the volume $V - v$ has escaped ("coagulated"); as this happened during t sec, the above expression for U_d results. In experiments on $0.004M$ aqueous p-toluidine solution, when t was 4, 8, 15.2, and 26.3 sec and v was 50, 90, 150, and 210 cm^3, U_d was 10.9, 5.5, 9.2, and 11.4 cm^3/sec, respectively. The volume V should be measured at, or recalculated to, the atmospheric pressure rather than at the higher pressure used to force the air through the porous membrane. The "average rate of static coagulation" is defined in section 30. A comparison of dv/dt and dV/dt for some frothers used in fire-fighting has been published by Clark[31].

Section 24. The *foam number* was defined by Lederer[29] as the volume of liquid transferred into foam by unit volume of gas. Hence, it really is a number (dimensionless). It is also possible to correlate the volume v_l of liquid in the foam with the amount m of solute present in the liquid[32, 33], i.e., to express the foaming capacity as v_l/m. These magnitudes may be expected to depend on the rate of gas flow, the apparatus dimensions, and the amount of liquid used, but no relevant experiments could be found in the literature.

Section 25. Foam can be produced by various kinds of *agitation*. Shaking is presumably the oldest and the easiest kind. As it is generally carried out in closed vessels, the disturbance due to evaporation is minimized. The height (or volume) of the foam column produced by shaking depends on the details of the movement imparted to the liquid, on the duration of shaking, on the apparatus dimensions,

and so on. Not many observations concerning these relations have been published.

Sasaki[34] could at will produce either a foam layer and a water-in-oil emulsion or an oil-in-water emulsion without any foam by changing the movement from swinging to up-and-down jerks; his system consisted of 2.33 cm^3 acetic acid, 3.79 cm^3 ether, and 3.88 cm^3 water in a stoppered test tube.

When the height of the liquid column (10 per cent glue solution) in the shaking tube rose from 5 to 25 cm, the foam height H rose from

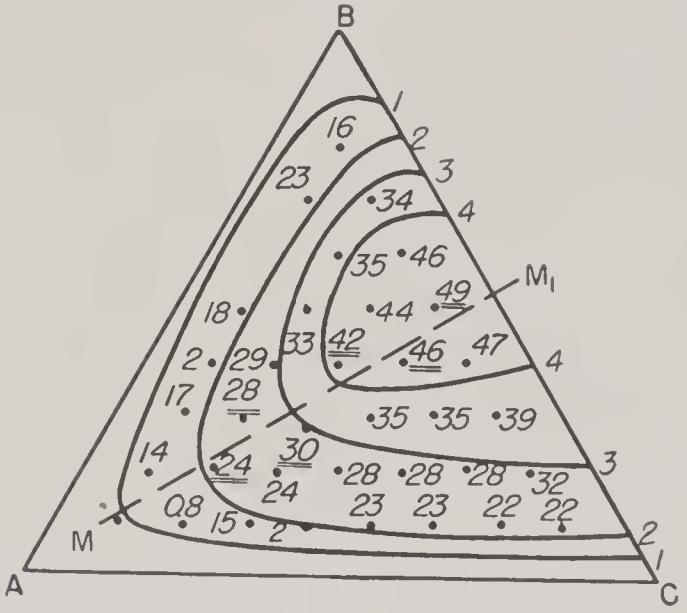


FIGURE 14. Dependence of foam height (after shaking) on the relative volumes of 0.1% gelatin solution (C), water (A), and air (B). The numbers represent the foam heights, and the solid lines connect systems having identical foam heights. From *Kolloidchem. Beihefte*, **31**, 418 (1930).

3 to 22 cm; it increased also when the depth of the liquid layer was increased by taking a narrower tube rather than a greater volume of the liquid[35]. Dumanskii[36] shook various volumes of aqueous gelatin solution of varying concentrations with air in a 100 cm^3 cylinder and found that H depended on the volume of air present. Fig. 14 shows his results. In the triangular diagram, A is pure water, C is 0.1 per cent gelatin solution, and B is air. The curves are drawn through systems having identical H, and line MM_1 connects the systems having highest H. It is seen that H was great when the volumes of air and of the 0.1 per cent gelatin solution were approximately equal, independently of the amount of water used to dilute the stock solution. When 50 cm^3 of a 0.14 per cent solution of soap flakes were shaken

with 70 instead of 145 cm^3 of air, foam height was increased by 25 per cent[37]; in this instance, however, the carbon dioxide of the air may have influenced the foaminess.

If all the factors mentioned in the first paragraph of section 25 are kept rigorously constant, reproducible values for the foam volume can be obtained. A standardized shaking procedure was adopted, for example, by the British Standards Institution[37a].

The "pour test" is closely akin to shaking. A standard volume (e.g., 200 cm^3) of solution is run through a standard funnel into a cylinder containing another constant volume (e.g., 50 cm^3) of the same solution, and the volume v of the froth formed is determined. This volume increases with the height from which the liquid fell[38]. For example, a 5 per cent solution of a commercial wetting agent gave v equal to 54, 42, and 22, respectively, (arbitrary units) when the drop was 297, 202, and 98 cm, respectively.[38] When a larger volume was run, v increased roughly proportional to it, and when the volume v_0 of liquid originally present in the cylinder increased, v first increased and then reached a value independent of v_0. As would be expected, this procedure was popular for testing beer[39]. However in beer the major part of the gas phase in the froth originates from the carbon dioxide dissolved in the beer, and the volume of liquid in the froth column is a linear function of the carbon dioxide content of the beer samples (see section 60). Instead of the solution, sand can be dropped onto the liquid surface; this method also has been used for beer[40].

Mechanical *beating* and *whipping* have been repeatedly applied. The kind of beating most like the method of Schuster and Mischke is moving a perforated plate up and down through the liquid-air interface. It is said[41] to have been adopted in the laboratories of I.-G. Farbenindustrie in 1937 and also was recommended recently[42]. The foam volume produced by it depends on the details of the experimental procedure[31]. Thus, for a 5 per cent commercial protein solution, the volume increased with the frequency of oscillations, e.g., in the ratio 2:1 when the frequency rose from 2 to 4 sec^{-1}. When the amount of liquid hit by the perforated plate was doubled, the foam volume increased in the ratio 1.3:1; this ratio depended also on the concentration of the solution. When oscillations were maintained for a longer time, the final foam volume was greater; it was, for example, 8 (arbitrary units) after beating for 10 min. and

11 after 90 min. In the experiments by Götte[41] this final volume reached an approximately constant value when the duration of beating was long enough; thus in 0.5 g/l solution of sodium palmitate at 60° the foam volume after

10	20	30	40	60	80	100 oscillations was
200	300	450	520	580	580	590 cm^3.

It has been claimed[43] that the height of foam produced by an oscillating perforated plate is better reproducible if the plate remains immersed in the liquid and thus does not move in (and damage) the foam. This was achieved in a vessel formed like a bottle upside down. The neck of this "bottle" contained the liquid, and the perforated plate never rose above the neck. The neck diameter (5.5 cm) was about one-half that of the main part of the vessel (11.5 cm), and its volume was one-eighth of the total volume. A cylinder of wire netting, 5.0 cm in diameter, was fixed around the axis of the vessel; thus the froth had to squeeze through the meshes before reaching the major part of the vessel (see section 6). The perforated disc had the dimensions specified by I.-G. Farbenindustrie, namely, diameter 4.8 cm, 30 holes of 0.3 cm each.

Electrically driven beaters and whippers of the household type are often used, especially for testing the foaming capacity of systems familiar in households. The difficulty of obtaining comparable results with these instruments may be illustrated by three examples. One "type of beater was found to be unsuitable for quantitative studies of the foaming power of egg white because the whipped white, by virtue of its stiffness, soon became immobilized around the beaters with the result that the blades rotated in a central cavity[44]". A wire whipper eccentrically situated on a rotating disc gave copious foam. Presumably both beaters would prove equally efficient in a system giving less stiff lamellae. Henry and Barbour[32] and others changed the density (see section 63) of egg white foams by changing the speed and duration of rotation of a kitchen beater. Ross[45] could not form any foam by beating aqueous ethylene glycol although identical solutions gave a tall and rather stable froth column in the pneumatic method (section 21). As the total volume of foam present in the bowl of a kitchen beater is not very easy to measure, the foam density often is determined instead.

In some flotation machines air is blown into the liquid as a jet

and then broken down to small bubbles by stirrers (see section 7). The overflow of foam in such a machine has been used as measure of the foaminess of the liquid[46].

Section 26. As mentioned in section 20, formation of foam by agitation consists of two distinct processes, namely (a) incorporation of gas in liquid and (b) rise of the gas surrounded by foam lamellae in and above the liquid. Only the second process is directly connected with the foaming capacity of the solution. However, the amount (or volume) of foam formed depends also on process (a), as the foam volume after shaking cannot be considerably greater than the volume of gas incorporated during shaking. This latter volume depends, in addition to the external variables (such as intensity of shaking, volume of the vessel, etc.), on some internal variables to which viscosity certainly and surface tension probably belong. Presumably, to obtain comparable results with two very different liquids, the agitation should be performed in such a manner that the Reynolds number would be constant rather than the vessel and the intensity of shaking. Reynolds number is $u\rho d/\eta$, u being a velocity, ρ density, d a length, and η viscosity. If, for example, u is kept constant and ρ is roughly identical for both liquids, d should be proportional to η; a solution in glycerol should be shaken in a tank 8 meters across to obtain conditions analogous to shaking aqueous solutions in a test tube 1 cm in diameter. (Viscosity of glycerol at room temperature is about 800 times that of water.) No experiments of this kind could be found in the literature.

Section 27. Foams produced by boiling can be measured in a manner very similar to that employed in the pneumatic method (section 21). The liquid to be tested is heated in a vessel (e.g., by immersed heaters), and the height or volume of the foam produced is read. In the pneumatic method the height increases with the rate of injection of air; analogously, in the boiling method, it increases with the amount of heat supplied in unit time or with the rate of evaporation[47, 48]. When, for example, the "steam upflow rate" increased from 2.5 to 6.1 cm/sec, the maximum foam height increased from 5 to 62 cm; no mathematical correlation between these two quantities has been established[48]. For comparing different solutions a

constant rate of rise of the vapor (e.g., 7 cm/sec) was used[49]. Whatever the conditions determining the bubble size in a boiling liquid small bubbles gave rise to a tall, and large bubbles to a low, foam column; when a coarse foam had to rise through a fine wire screen, the foam height increased[49].

Different substances can be compared by determining those concentrations of their solutions which gave a predetermined height of foam on boiling in a standard beaker[50].

A correlation between the foam volumes produced by bubbling and by boiling would be expected if the bubbling is conducted at a temperature almost equal to that of boiling. If foaming of a boiling liquid is compared with that of the same liquid at a quite different ("room") temperature, large discrepancies are likely to appear. This was observed, for example, by Gunderson and Denman[51]: impure water which did not foam in a yard locomotive gave foam persisting for over 3 weeks on shaking in a bottle in the laboratory.

In experiments on boiling, the carry-over or priming is often determined. Carry-over is the amount of liquid which reaches the condenser without passing through the vapor state. If the boiling liquid (as is the rule) contains dissolved nonvolatile substances, their concentration in the condensed liquid is a direct measure of the carry-over. This concentration can be measured in any conventional manner, but it gives only an inexact idea of the extent of foaming, as carry-over can be caused also by other effects, (see, e.g., ref. 52). Durov[53] determined the amount a_1, which distilled in, say, 5 min. at a constant heat input and a constant pressure, and then lowered the pressure by, say, 300 mm Hg. In the next 5 min. the amount of liquid in the receiver increased by a_2. The difference $a_2 - a_1$ was the carry-over. The boiler was of glass, and it could be seen that, when $a_2 - a_1$ was large, the liquid was thrown into the condenser without passing through the stage of foam.

Section 28. By whatever method the foam has been produced, it starts to *collapse* as soon as the injection of gas ceases. This collapse should not be confused with drainage (see section 53). The height h or the volume v of the foam is measured at once after the discontinuation of the bubbling, shaking, etc., and then at regular intervals. Then h or v is plotted as a function of time t, or the relation between v and t is expressed by an equation (see, e.g., refs. 54 and 54a).

It was also suggested[55] to determine the area under the $h - t$ curve and to divide it by the original height h_0 (i.e., at $t = 0$); the resulting quantity was termed the average lifetime of gas in the foam and represented by sign L_g.

The form of the equation connecting v and t, if known, would be of great importance for the elucidation of the mechanism of rupture of foam bubbles. For the sake of simplicity assume the foam to be isotropic, i.e., to show no difference between top and bottom, center and periphery, etc. If the stability of the bubble does not depend on its age, that is, if a fresh bubble is as likely to burst as an aged one, then the number n of bubbles will decay according to the exponential function $n = n_0 e^{-mt}$, n_0 being the original number and m a constant. If the bubble is most likely to burst when it is Σ sec old, and the probability of bursting decreases at greater and smaller t according to the normal distribution curve, then

$$n = \frac{n_0}{\sigma\sqrt{2\pi}} \int_0^t \exp.\,[-(t - \Sigma)^2/2\sigma^2]\, dt,$$

σ being the standard deviation. In this case, n as function of t would form an inverse S-shaped curve: a slow decrease as long as the few short-lived bubbles burst, then an almost linear rapid decrease including an inflexion point, and finally another slow decrease when the few remaining oldsters pass away. Other hypotheses concerning the nature of bursting will lead to other equations between n and t (see also Chapter 9).

The experimental material does not allow any decision on the probable mechanism of rupture. The curves shown in Lubman's paper[56] for aqueous solutions of isoamyl alcohol, α-naphthylamine, and m-cresol are not sufficiently explained in the paper. Often the rate of collapse of Lubman's foams decreased in time during an experiment and reached a very small value when the foam column still was as high as 1 cm. The data published by Smirnov and Bondarenko[57], by Sauer and Aldinger[58], by Ostwald and Steiner[59], and by Kionka[60] refer to liquids of imperfectly known chemical compositions (treated sulfite liquor, animal glue, humic acid, and commercial soap, respectively). As an example, the foam volumes of the best and the least foaming 10 per cent glue solution were 84.0, 70.3, and 64.0 cm^3 and 6.1, 5.0, and 3.3 cm^3 respectively, 1, 3, and 5 min. after shaking[58]. Kionka's values for 1 per cent soap solutions are 19.1,

18.8, 17.3, 12.1, 7.9, and 3.9 cm foam height after 5, 10, 15, 120, 210, and 360 min.

Fig. 15 from Brady and Ross[55], curve *a*, shows the decay of foam of a 2 per cent solution of $CH_3(CH_2)_4CH(CH_3)CH_2 \cdot O \cdot CO \cdot CH_2$-$CH(SO_3Na)CO \cdot O \cdot CH_2CH(CH_3)(CH_2)_4CH_3$ in triethanolamine at 100°, while curve *b* is that of drainage. In their experiments on lubricating oils, the $v - t$ curve of a foam produced by shaking had the inverted S-shape. The authors did not correlate it with probability but rather attributed the slow collapse during the initial stage to the high percentage of water in the fresh foam. (This explanation is, of

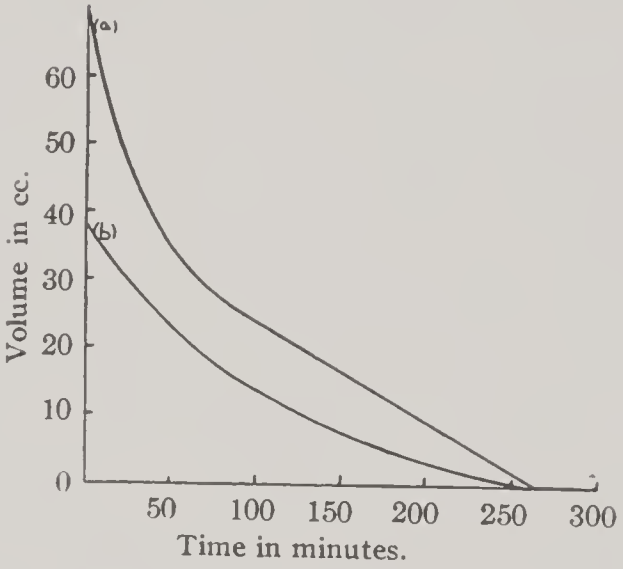


FIGURE 15. Decay of foam of 2% "Aerosol OT" in triethanolamine at 100°, bubbling method: (a) gas in foam; (b) liquid in foam.

course, wholly consistent with the probability considerations.) A foam of the same oil, obtained by bubbling, decayed linearly with time.

Section 29. Instead of the whole $v - t$ curve many experimenters determined only two points on it, i.e., they measured v at the beginning of collapse and, say, 10 min. later[25] or noted the time required for the foam to be reduced to a small, more or less definite volume. Lubman[56], Aleĭnikov[22] and others took the moment of the appearance of the free liquid surface as the end point ("because bubbles adjacent to the wall of the cylinder exhibit great stability"). Robinson and Woods[61] and Teĭtelbaum[62] waited until just two bubbles remained.

Other authors give values for "the time of collapse" without defining it more closely.

It is clear that in all these procedures the persistence of one and only one bubble is determined (see also section 19). An analogous method would be to estimate the death rate of a population from the age of the oldest (or the third-oldest) inhabitant who died last year. The "time of collapse" will be particularly misleading if the foam has been produced by shaking. The time of collapse, as a rule, will be longer the more bubbles there are in the foam (see section 30), just as the age of the oldest inhabitant increases the more numerous the population surveyed. In its turn, the original number of bubbles depends on the viscosity (and probably surface tension) of the solution (see section 26). Hence the time of collapse of a viscous liquid may be small simply because the "standard" shaking produced but few bubbles. The same liquid in another test (e.g., of the persistence of single bubbles, section 19) would appear to have a great foaminess.

Nakagaki[63] determined the original height of the foam column after shaking (H), the time required for the liquid surface to appear (t_1), and the time required for disappearance of the most persistent bubble ($t_1 + t_2$). When the composition of the solution (mixture of water, ethyl alcohol, and glycerol) was varied, H and t_1 changed more or less in the same direction, but the variations of t_2 often had the opposite sign. In these experiments the lifetime of two bubbles was determined.

Section 30. If the original foam volume was v_1 and free liquid surface appeared after t_1 sec, then v_1/t_1 is the "average rate of static coagulation."[22] This quantity would be nearer to being a physical property of the solution the less its dependence on v_1. Savitskaya and Rebinder[64] made monodisperse foams by collecting bubbles rising from one capillary. For such foams of 0.37 per cent solution of sodium 6-butylnaphthalene-1-sulfonate, v_1/t_1 was independent of v_1 in nearly saturated vapor. However, t_1 depended on the environment in which the collapse took place just as much as the other measures of stability (see section 18). A 12 cm tall foam column collapsed within 7 min. in air, 62 min. in nearly saturated vapor, and 282 min. in the absence of the continuous gas phase. The last mentioned system was achieved by releasing air bubbles under an inverted beaker immersed in the solution and equilibrated with a weight. The froth gradually displaced the liquid from the beaker and was thus confined between

the bottom part of the beaker and the surface of the solution. When froth columns of equal height but different areas (formed in vessels of varying diameters) were compared, it was found that t_1 little depended on the diameter when this was large (over 4 cm) but was 4 times as great in a 1 cm wide vessel. The t_1 of monodisperse froth of 1 per cent sodium dioctyl sulfosuccinate, in an open space, rapidly decreased when the bubble diameter ($2R$) increased; it was about 1,000 sec when $2R$ was 1 mm and about 20 sec at $2R$ = 10 mm (see also section 19). In closed space, t_1 but little depended on $2R$; it was, for example, 48 hours at $2R$ = 0.04 mm and 22 hours at $2R$ = 10 mm. The values for the bubble diameters are only approximate but the great difference between the behaviors in open and closed space will not be obviated by the error thus made.

The "rate of static coagulation" may be compared with the "rate of dynamic coagulation" as defined in section 23. For the four foams of 0.004M *p*-toluidine mentioned there, v_1/t_1 was 3.1, 4.8, 8.2, and 11.5 cm^3/sec, respectively. Thus for the two largest foams (of 150 and 210 cm^3), v_1/t_1 was almost equal to the "rate of dynamic coagulation." A similar approximate agreement was observed also for some other solutions[22].

For three lubricating oils, L_g (see section 28) was (at 26°) 79, 104, and 27 min., respectively[55]. For the same oils, Σ (see section 22) was measured and found to be (at 56°) 7, 10, and 4 min., respectively. The parallelism between the two magnitudes is unmistakable. Further work on this relation would be welcome.

A magnitude akin to the time of collapse has been determined by Hancock[65] for foams produced by boiling. When the pressure above a boiling liquid is suddenly reduced, the foam volume rapidly increases to a maximum value. Then, when the boiler is closed and the pressure in it is gradually built up, the foam shrinks "to its original thickness." The time required for this shrinkage was, for example, 1.4 sec for distilled water and 5 sec for a (nonspecified) soap solution.

References

1. Plateau, J., *Mém. acad. roy. sci. Belgique*, **33** (1861). 5th ser.
2. Foulk, C. W., and Barkley, J. E., *Ind. Eng. Chem.*, **35**, 1013 (1943).
3. Plateau, J., *Mém. acad. roy. sci. Belgique*, **36** (1867). 7th ser.
4. Bikerman, J. J., *J. Phys. Chem.*, **56**, 164 (1952).
5. Smirnova, A. M., and Rebinder, P. A., *Compt. rend. acad. sci. U.R.S.S.*, **52**, 317 (1946).
6. Stokes, A. J., U. S. Patent 2,473,553; *Chem. Abs.*, **43**, 6764 (1949).

7. Sameshima, J., Nakamuta, M., and Terada, R., *J. Chem. Soc. Japan*, **63,** 691 (1942); *Chem. Abs.*, **44,** 10414 (1950).
8. Matalon, R., *Compt. rend.*, **227,** 634 (1948); *Research (London), Suppl. Surface Chemistry*, **1949,** p. 195.
9. Plateau, J., *Mêm. acad. roy. sci. Belgique*, **37** (1869). 9th ser.
10. Dewar, J., *Proc. Roy. Inst. Gt. Brit.*, **21,** 786 (1916).
11. Rehbinder, (Rebinder), P., and Wenström (Venstrem), E., *Kolliod-Z.*, **53,** 145 (1930).
12. Rodewald, H. J., *Naturwissenschaften*, **37,** 284 (1950).
13. Hardy, W., *J. Chem. Soc.*, **127,** 1207 (1925).
14. Mentioned by I. W. Wark, "Principles of Flotation," p. 282, Australian Inst. Mining Metallurgy, 1938, Melbourne.
15. Talmud, D., and Sukhovolskaya (Suchowolskaja), S., *J. Phys. Chem. (U.S.S.R.)* **2,** 31 (1931); *Z. physik. Chem.*, **154A,** 277 (1931).
16. Foulk, C. W., and Miller, J. M., *Ind. Eng. Chem.*, **23,** 1283 (1931).
17. Hazlehurst, T. H., and Neville, H. A., *Ind. Eng. Chem.*, **31,** 1084 (1941).
18. McBain, J. W., and Robinson, J. V., Natl. Advisory Comm. Aeronaut., Tech. Note No. 1844 (1949).
19. Schütz, F., *Trans. Faraday Soc.*, **38,** 85 (1942).
20. Šandera, K., and Miřčev, A., *Listy Cukrovar.*, **51,** 83 (1932); *Chem. Abs.*, **27,** 2328 (1933).
21. Taggart, A. F., and Gaudin, A. M., *Trans. Am. Inst. Min. Met. Eng.*, **68,** 479 (1923).
22. Aleinikov (Alejnikoff), N. A., *Tsvetnye Metally*, **6,** 1546 (1931); *Kolloid-Beihefte*, **36,** 82 (1932).
23. Bikerman, J. J., *Trans. Farad. Soc.*, **34,** 634 (1938).
24. Clark, G. L., and Ross, S., *Ind. Eng. Chem.*, **32,** 1594 (1940).
25. Am. Soc. Testing Materials Book of Standards, 1946, III A, p. 853, Method D 892 – 46 T.
26. Sasaki, T., *Bull. Chem. Soc. Japan*, **13,** 517 (1938).
27. Dyakonov, G. K., *J. Tech. Phys. (U.S.S.R.)*, **12,** 302 (1942); *Chem. Abs.*, **37,** 5299 (1943).
28. Pattle, R. E., *J. Soc. Chem. Ind.*, **69,** 369 (1950).
29. Lederer, E. L., *Z. angew. Chem.*, **47,** 119 (1934).
30. Sinsheimer, J. G., *Soap Sanit. Chemicals*, **26,** No. 8, 38 (1950).
31. Clark, N. O., "A study of Mechanically Produced Foam for Combatting Petrol Fires," Dept. Sci. Ind. Research, London, 1947.
32. Henry, W. C., and Barbour, A. D., *Ind. Eng. Chem.*, **25,** 1054 (1933).
33. Perri, J. M., and Hazel, F., *Ind. Eng. Chem.*, **38,** 549 (1946); *J. Phys. & Colloid Chem.*, **51,** 661 (1947).
34. Sasaki, T., *Bull. Chem. Soc. Japan*, **14,** 63 (1939).
35. Trotman, S. R., and Hackford, J. E., *J. Soc. Chem. Ind.*, **25,** 104 (1906).
36. Dumanskii, A., *Kolloidchem. Beihefte*, **31,** 418 (1930).
37. Hetzer, *Chem. Ztg.*, **57,** 715 (1937).
37a. British Standard Specification No. 844–1939.
38. Ross, J., and Miles, G. D., *Oil & Soap*, **18,** 99 (1941).
39. Helm, E., and Richardt, O. C., *J. Inst. Brewing*, **42,** 191 (1936).

40. Schuster, K., and Mischke, W., *Wochschr. Brauerei*, **54**, 177 (1937); *Chem. Abs.*, **32**, 1396 (1938).
41. Götte, E., *Melliand Textilber.*, **29**, 65, 105 (1948).
42. Noll, A., *Seifensieder-Ztg.*, **73**, 41 (1947); *Chem. Abs.*, **42**, 3976 (1948).
43. Schlachter, A., and Dierkes, H., *Fette u. Seifen*, **53**, 207 (1951).
44. Bailey, M. I., *Ind. Eng. Chem.*, **27**, 973 (1935).
45. Ross, S., *J. Phys. Chem.*, **50**, 391 (1946).
46. Mortenson, M., *Kgl. Norske Videnskab. Selskabs. Forh.*, **7**, 11 (1935); *Chem. Abs.*, **29**, 4709 (1935)
47. Eberle, C., *Arch. Wärmewirt.*, **10**, 329 (1929); *Chem. Abs.*, **24**, 5897 (1930).
48. Leaf, W., *et al.*, *Am. Ry. Eng. Assoc.*, **46**, *Bull.* **448**, 59 (1944).
49. Leaf, W., *et al.*, *Am. Ry. Eng. Assoc.*, **45**, *Bull.* **441**, 58 (1943).
50. Kollmann, L., *Textil-Betrieb* (Nov. 1938), p. 16; *Chem. Abs.*, **33**, 1951 (1939).
51. Gunderson, L. O., and Denman, W. L., *Ind. Eng. Chem.*, **40**, 1363 (1948).
52. O'Connell, H. E., and Pettyjohn, E. S., *Trans. Am. Inst. Chem. Engrs.*, **42**, 795 (1946).
53. Durov, S. A., *J. Applied Chem. (U.S.S.R.)*, **13**, 693 (1940).
54. Constable, F. H., and Erkut, H., *Rev. faculté sci. univ. Istanbul* **A12**, No. 1, 38 (1947); *Chem. Abs.*, **41**, 4993 (1947).
54a. Maltepe, A. H., *Bull. Turkish Phys. Soc.*, No. 5 (undated); *Chem. Abs.*, **46**, 6461 (1952).
55. Brady, A. P., and Ross, S., *J. Am. Chem. Soc.*, **66**, 1348 (1944).
56. Lubman, N. M., *Tsvetnye Metally*, **6**, 854 (1931).
57. Smirnov, V. A., and Bondarenko, A. N., *J. Applied Chem. (U.S.S.R.)* **20**, 97 (1947).
58. Sauer, E., and Aldinger, W., *Kolloid-Z.*, **88**, 329 (1939).
59. Ostwald, Wo., and Steiner, A., *Kolloid-Z.*, **36**, 342 (1925).
60. Kionka, H., *Z. deut. Öl-u. Fett-Ind.*, **43**, 467 (1923).
61. Robinson, J. V., and Woods, W. W., *J. Phys. & Colloid Chem.*, **52**, 763 (1948).
62. Teitelbaum, B. Ya., *Kolloid. Zhur.*, **12**, 375 (1950).
63. Nakagaki, M., *Bull. Chem. Soc. Japan*, **21**, 30 (1948).
64. Savitskaya, E. M., and Rebinder, P. A., *Doklady Akad. Nauk S.S.S.R.* **76**, 427 (1951); *Kolloid. Zhur.*, **13**, 200 (1951).
65. Hancock, J. S., *J. Soc. Chem. Ind.*, **49**, 369T (1930).

3. RESULTS OF FOAMING MEASUREMENTS

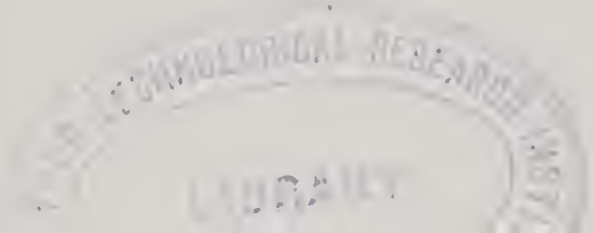
Section 31. If a single value independent of the apparatus and method used could be established for the foaminess of a liquid (at specified temperature and other external parameters), then this chapter would have consisted of tables such as are given in more fortunate books for surface tension, viscosity, and analogous physical quantities. Compilation of such tables for foaminess is impossible in the present state of our knowledge, and the values presented below may claim validity only for the particular instrument and the particular procedure employed.

In sections 32–42, foaming capacities are listed according to the chemical composition of the frothing liquid and some rules for the relation between foaminess and composition are formulated. From Chapter 9, particularly section 95, it will be clear that these rules cannot have a quite general validity.

Foaminess and Chemical Composition

Section 32. Pure liquids do not foam and saturated solutions foam, if at all, very poorly. This rule has been established by numerous observations, and many instances of its validity can be found below. Plateau's list[1] of liquids whose surfaces do not stop single bubbles (see section 19) consists of pure liquids (water, glycerol) and saturated aqueous salt solutions (of KNO_3, $CaCl_2$, Na_2CO_3, etc.). However, the reliability of Plateau's results suffers because he had no means of cleaning his surfaces; the weak foaming observed by him in glacial acetic acid, ethanol, chloroform, ether, and so on presumably was caused by impurities.

Foulk and Barkley[2] performed special experiments to prove the first part of the above rule. They used the instruments illustrated in Fig. 10 and discussed in sections 17 and 19. Ordinary distilled water yielded films in a platinum ring 8 times out of 100; after another distillation the percentage was reduced to 4, and after distillation from potassium permanganate and potassium hydrogen sulfate, to zero. A sample kept in air for 12 hours gave 58 per cent. In non-



aqueous liquids water seemed to be the chief cause of foaminess, and its elimination eliminated foaming as well. Benzene and *n*-heptane lost their film-forming capacity (or almost all of it) after distillation over sodium, methanol after distillation over magnesium, and acetone, over anhydrous potassium carbonate. Nitrobenzene and ether did not foam in their ordinary state of purity but did after some water (0.1 and 0.02 per cent) was added.

As neither pure liquids nor saturated solutions foam, a maximum of foaming capacity should occur at some medium concentration. Numerous instances of this behavior are presented in the following.

Section 33. *Inorganic compounds in aqueous solution.* Not much information is available on foaminess of aqueous solutions of inorganic

TABLE 3. PERSISTENCE (IN SEC) OF SINGLE BUBBLES, 0.15 CM IN DIAMETER

	KSCN	NaOH	KBr	KCl	$K_3Fe(CN)_6$	K_2SO_4	$AlCl_3$
0.05*N*	—	3.8	6.6	0.0	8.3	3.0	11.3
0.1*N*	—	16.5	20.4	10.0	11.3	17.0	36.4
0.4*N*	—	—	20.0	19.3	—	—	71.6
0.8*N*	0.5	—	19.1	24.3	—	—	—
1.0*N*	—	15.2	—	—	39.7	40.0	—
1.6*N*	11.7	—	17.7	21.0	—	—	—

compounds. Generally, this foaminess is quite small compared with that shown by aqueous solutions of many alcohols and organic acids, bases, and salts. A half-inorganic salt, namely ferric acetate, was listed by Plateau[1] as strongly foaming.

The lifetimes of single bubbles (section 19) in the surface of some salt solutions are listed in Table 3 from ref. 3. If these solutions are compared at equal normalities, the persistence seems generally to increase from KSCN to NaOH < KBr < KCl < $K_3Fe(CN)_6$ < K_2SO_4 < $AlCl_3$, although the order of salts varied depending on concentration. The sequence of anions (from SCN to SO_4) reminds one of the lyotropic series. The less tendency an anion has to increase the surface tension of water, the less persistent the foam is in the solutions of its salts.

At the concentration of 2.57 g/l, the foam heights of boiling sodium sulfate, sodium carbonate, and sodium hydroxide solutions, for the rate of rise equal to 5.67 cm/sec, were 2.5, 10.2, and 7.6 cm, respectively[4]. The time of collapse (section 30) of foam on a boiling 0.2 per cent solution was 5.8 sec for sodium hydroxide, 4.6 sec for potas-

sium hydroxide, 2.6 sec for potassium chloride, and 1.6 sec for potassium nitrate[5]. In this test caustic alkalis appeared to be better frothers than neutral salts. However, the possibility should be borne in mind that alkalis formed soap-like compounds with some impurities in the solvent.

The foaming capacity usually increases with concentration, as long as this is moderate. This can be deduced from Table 3 and was observed also for foams produced by boiling. The foam height above boiling solutions of the salt mixture sodium sulfate 75 per cent, sodium hydroxide 12.5 per cent, sodium carbonate 12.5 per cent (weight per cents) was greater the greater the concentration within the range 1.7–5 per cent approximately, but was nearly independent of concentration above this range[6]. In boiling sodium chloride solutions[7] the foam height increased up to 4 per cent sodium chloride, became either independent of concentration or passed through a flat maximum between 4 and 8 per cent sodium chloride, and decreased when the concentration was pushed to 15 per cent. The time of collapse[5] for boiling 1 per cent potassium chloride and potassium nitrate solutions was 4.4 and 2.8 sec, respectively, i.e., about 1.7 times that of 0.2 per cent solution.

It is instructive to compare the absolute data for sodium hydroxide, the only substance studied by three different methods. For 0.2 per cent solutions the time of collapse at boiling temperature was 5.8 sec and the persistence of single bubbles at room temperature was 3.8 sec, while for 0.257 per cent solution the ratio h/u (section 22) at boiling temperature was 1.1 sec.

If a solution contains more than one inorganic solute, its foaming capacity is no simple function of the foaming capacities of the constituents. Durov[8] published a triangular diagram showing the carry-over in the system sodium carbonate, magnesium chloride, calcium chloride (and water); it is reproduced in ref. 9, p. 102. An analogous diagram for foam height above boiling liquids is given here as Fig. 16 from Leaf[4]. The figures must be multiplied by 2.54 to obtain foam heights in cm and by 0.373 to obtain the ratio h/u in sec. All solutions contained 2.57 g solid substance in liter.

Fesenko[8a] measured the carry-over of boiling solutions in an iron flask. Each solution contained three dissolved electrolytes, namely sodium hydroxide, sodium carbonate, and sodium chloride, or sodium hydroxide, sodium carbonate, and sodium sulfate. The total concentration varied between 0 and 120 milliequivalents/liter. In both

systems the carry-over increased with the total concentration. In the first system it was particularly great when the mole fraction of sodium chloride, and in the second when the mole fraction of sodium carbonate was small.

The foaminess of sea water usually is not due to its salt content but rather to organic impurities (see section 110). Thus "artificial sea

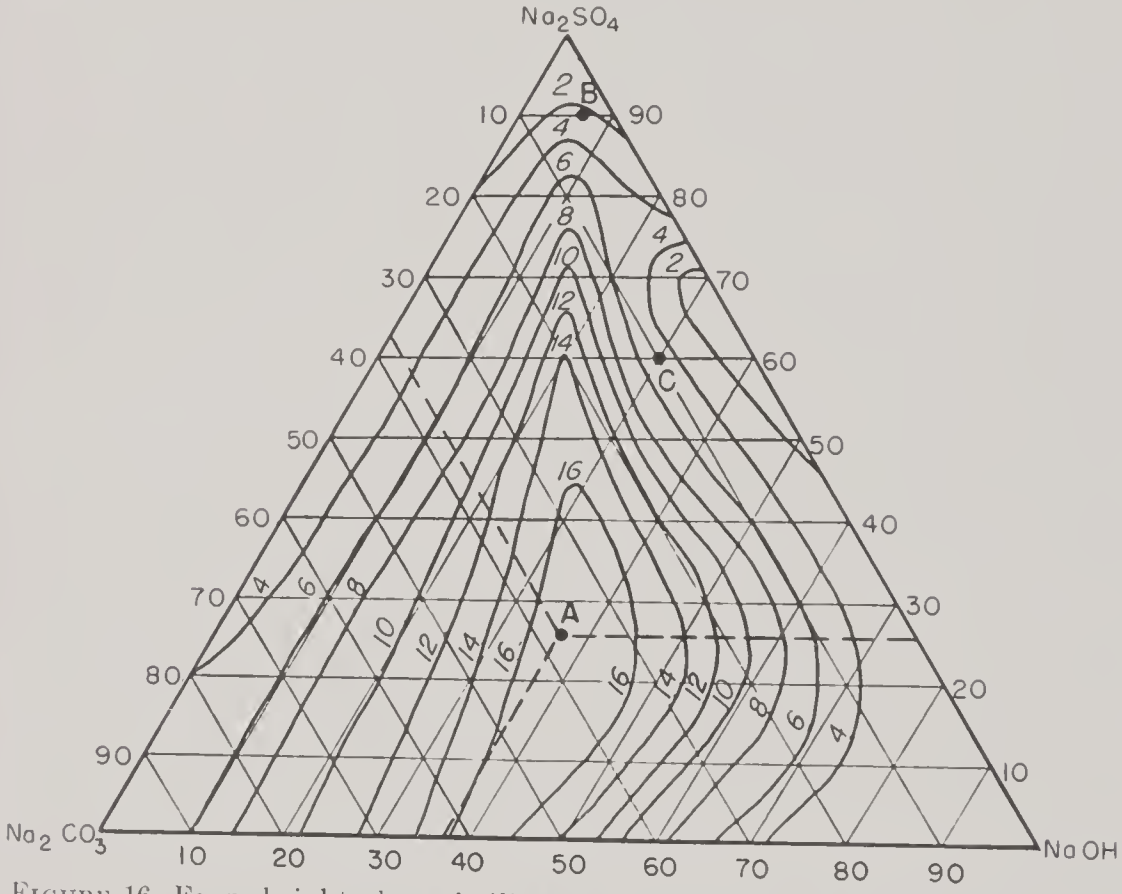


FIGURE 16. Foam height above boiling solutions (2.57 g/l) of sodium sulfate, sodium carbonate, and sodium hydroxide. Numbers outside: weight per cents of the components. Numbers inside: foam heights in inches. From *Am. Ry. Eng. Assoc.*, **45**, *Bull.* **441**, 58 (1943).

water", i.e., an aqueous solution (in the right concentration) of the main salts present in the ocean, had a smaller foam height after shaking than natural ocean water which gave a foam almost as voluminous as 0.8*M* acetic acid[Sb].

Section 34. *Aqueous solutions of alcohols.* The persistence of foam in these solutions has a distinct maximum at some concentration which depends on the nature of the alcohol, the purity of the sample,

and the method of measurement. Table 4 summarizes the main data available for the position of these maxima. The persistence of single bubbles (section 19), the time of collapse of froth after shaking (usually the time required for the liquid surface to appear (see section 29), and the ratio h/u (section 22) in the pneumatic method are listed in separate columns. They all are expressed in seconds. The last column brings additional references to papers containing experimental results on the foaming capacity of the particular alcohols. The concentrations cannot be given in consistent units throughout as no densities have been determined by the authors. However, the three units used (per cent weight to weight, per cent weight to volume, and per cent volume to volume) do not differ by more than 20 per cent, while the table shows that the differences between the results of different authors were much greater than this. Undoubtedly these discrepancies are due not only to the absence of standardized methods of measurement but also to the variable purity of the alcohols used. It is hoped that more attention will be paid to this factor in future. In recalculating the values found by Gibb and Htin[12] it was assumed that the "height of froth" of the original includes the liquid layer as well.

In spite of the disheartening inconsistency of the data, Table 4 allows some conclusions to be made. The maximum persistence increases with the molecular weight up to C_5 or C_6 and then decreases again. The reason for this decrease is discussed in section 42 together with the reason for the maximum of foaminess at a medium concentration. The concentration (in volume per cent, in weight per cent, or also in molarities) corresponding to this maximum is smaller the greater the molecular weight. If n is the number of carbon atoms in the alcohol, this concentration (per cent v. v) is said to be ab^n, a and b being constants[10].

Three isomeric amyl alcohols (not specially purified) had similar times of collapse [10]. However, in Bartsch's experiments[14] the maximum time of collapse of isoamyl alcohol (17 sec) was significantly greater than that of tertiary amyl alcohol (1.1-dimethylpropanol) (10 sec).

For cetyl alcohol, see section 41.

Fig. 17 illustrates the concentration dependence of the foaminess of aqueous alcohol solutions. It combines data of Rebinder and Venstrem[17] for isoamyl alcohol (single bubbles from an orifice 0.051 cm in diameter, open vessel) with those of Lubman[18] (also for isoamyl alcohol but using the time of collapse after shaking) and those of

Table 4. Maximum Persistence of Foam of Aqueous Alcohols and the Concentration Corresponding to This Maximum

Alcohol	Single Bubbles	Ref.	Time of Collapse after Shaking	Ref.	Pneumatic h/u	Ref.	Ref.
Methanol			3 sec; 90% v/v	10	4.7 sec; 3.5% w/w	12	
			1.5 sec; 10% w/w	11			
Ethanol	15 sec; 3% w/w (closed space)	3	2 sec; 35% w/w	11	1.6 sec; 5% w/v	15	
			4 sec; 10% v/v	10	8.4 sec; 2.5% w/w	12	
			5 sec; 1.3% w/v	14			
			7 sec; 5% v/v	13			
1-Propanol			11 sec; 2.6% w/v	14			
			22 sec; 15% v/v	10			
2-Propanol			18 sec; 0.7% v/v	10	14.5 sec; 1.5% w/w	12	
1-Butanol			31 sec; 1.8% v/v	10	6.2 sec; 1% w/v	15	16
					24.5 sec; 0.4% w/w	12	
2-Butanol					20.5 sec; 0.35% w/w	12	
2-Methylpropanol			12 sec; 0.67% w/v	14	22.3 sec; 0.375% w/w	12	
			10–17 sec: ?	10			
1-Pentanol			52 sec; 0.97% v/v	10	6.6 sec; 0.12% w/v	15	
2,2-Dimethylpropanol					17.6 sec; 0.25% w/w	12	
3-Methylbutanol	53 sec; 0.33% w/v (open space)	17	17 sec; 0.32% w/v	14	25.9 sec; 0.20% w/w	12	19
			17 sec; 0.53% w/v	18			
			25 sec; 0.44% w/v	17			
			2500 sec; 1.96% v/v	10			
1-Hexanol			? sec; 0.33% v/v	10	7.9 sec; 0.36% w/v	15	
1-Heptanol			8 sec; 0.0081% w/v	14			
			? sec; 0.051 % v/v	10			
1-Octanol			5 sec; 0.004% w/v	14	2.6 sec; 0.013% w/v	15	20
			? sec; 0.011% v/v	10			

Sasaki[15] (for *n*-butyl alcohol and the pneumatic method). The two curves for isoamyl alcohol are similar. Quantitative agreement of the two sets of persistence values cannot be expected, as the magnitudes measured were different, the bubble size was not controlled, the rates of evaporation differed, and so on. No theory accounting in detail for the shape of the persistence-concentration curves could be found in the literature, except for the paper by Nakagaki[21] who

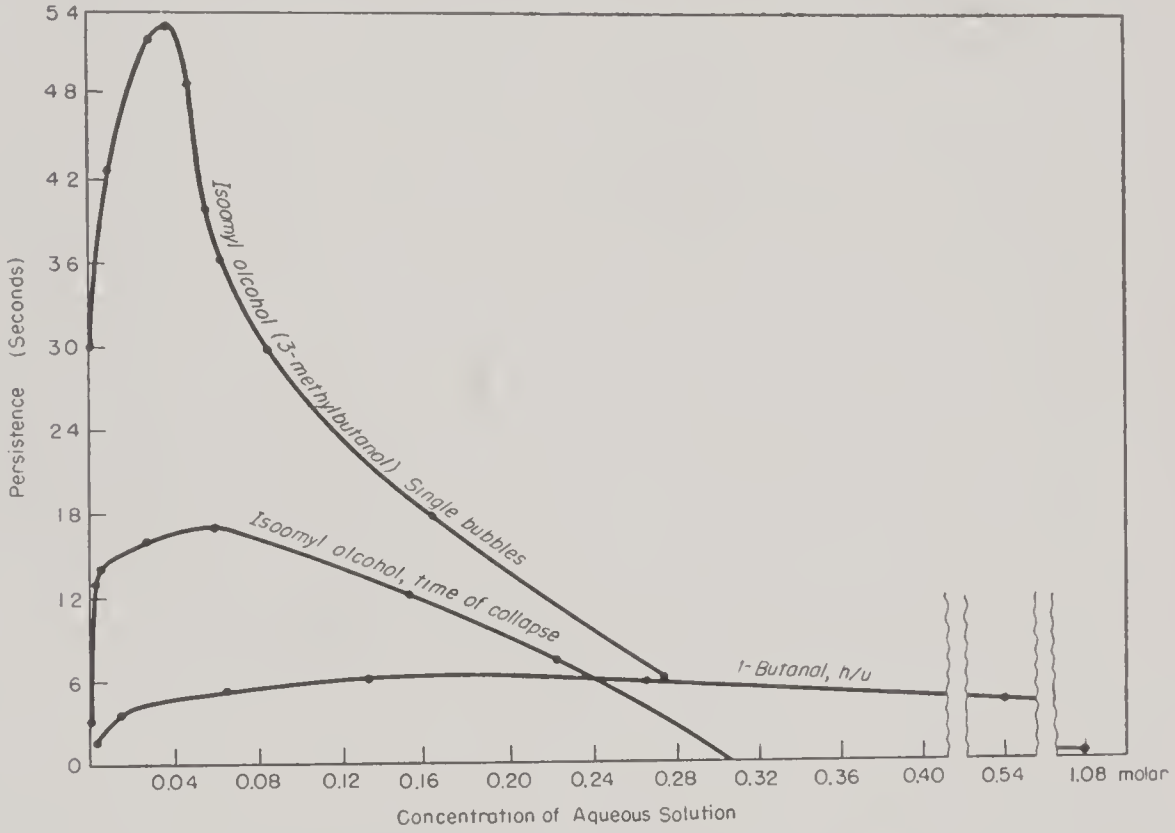


FIGURE 17. Foam persistence of 3-methylbutanol and 1-butanol solutions as a function of concentration. Data of Rebinder and Venstrem[17], Lubman[18], and Sasaki[15].

pointed out the similarity between these curves and the concentration dependence of the energy required to remove unit area of adsorption layer from the surface of the solution; unfortunately, calculation of this energy is not possible without some uncertain assumptions.

Solutions of two alcohols in water have been little studied. Nakagaki[11] published triangular diagrams for the height and time of collapse of foams produced by shaking water-ethanol-methanol mixtures.

Electrolytes slightly reduce the time of collapse of isoamyl alcohol foams. The range of the electrolyte concentration within which this reduction is most marked depends above all on the valency of the

cation. Thus it is 0.001 to 0.01N for sodium chloride and potassium thiocyanate, 0.0008 to 0.012N for sodium sulfate, and 0.0018 to 0.003N for sodium citrate, while the values for bivalent cations (barium chloride and magnesium sulfate have been tested) were between 0.000015 and 0.0005N, and the values for aluminum chloride and ferric chloride one-hundredth of those for magnesium sulfate and barium chloride. Further increase of the electrolyte concentration caused no additional acceleration of the foam collapse[14].

Section 35. *Aqueous solutions of other hydroxy compounds.* The persistence of air in foam (i.e., h/u, section 22) and the time t of collapse after bubbling depend on the concentration of aqueous solutions of glycol in a similar manner[22]. With glycol which was not specially purified both had maxima in the mixture of glycol 30, water 70 weight per cent; t was approximately 25 sec. After the glycol was purified, the maximum moved to 5 per cent glycol solutions, and both h/u and t somewhat decreased. In Bartsch's experiments[14] the greatest t was 1.5 sec and observed in 6M solution (containing 37 g glycol in 100 cm^3 solution).

In the system water-glycerol the time of collapse (not exactly defined) had a maximum (3 sec) again in 6M solution (i.e., at 55 g glycerol in 100 cm^3 solution)[14]. The time t_1 for the liquid surface to appear (see section 29) had a maximum (7 sec) at 15 per cent w/w while the lifetime of the most persistent bubble ($t_1 + t_2$) had a subordinate maximum (14 sec) at the same concentration but also a much taller maximum (128 sec) in 88 per cent glycerol[23].

According to Bartsch[14] both phenol and benzyl alcohol have a maximum of t in 0.1M solutions; it was 12 sec for phenol and 10 sec for benzyl alcohol.

For *m*-cresol three series of measurements of the time of collapse are available. In one[19], 100 cm^3 of air were introduced through a sintered glass plate into the solution in an open tube, and the foam allowed to collapse; thus during both formation and collapse the foam was exposed to dust and to evaporation. In the other two[14, 18], the foam was produced by shaking, i.e., in a closed vessel. Fig. 18 demonstrates the striking difference of the results obtained. The disagreement between the absolute values of the persistence may be due partly to the different starting volumes of the foam (Bartsch shook 10 cm^3 solution with about 30 cm^3 air, while Lubman employed

25 cm^3 solution and about 25 cm^3 air). However, the presence of definite maxima on the curves obtained in closed vessels and the absence of a sharp maximum in an open vessel may be due to evaporation (see section 19).

In an open vessel the time of collapse of *o*-cresol foam seems to have

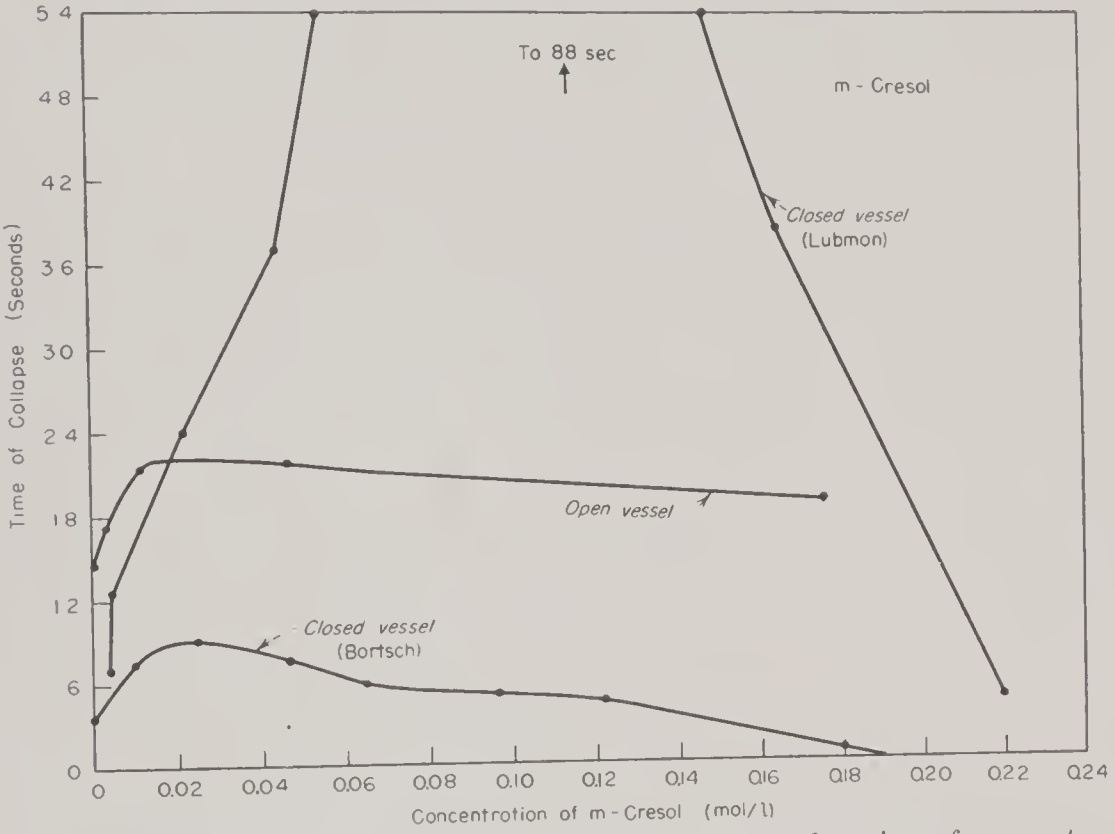


FIGURE 18. Time of collapse of *m*-cresol solutions as a function of concentration. Data of Bartsch[14], Lubman[18], and Alcinikov[19].

TABLE 5. EFFECT OF NaOH ON THE TIME OF COLLAPSE OF 0.11*M* *m*-CRESOL SOLUTIONS

Mol. ratio, NaOH:cresol	0	0.04	0.08	0.39	3.9
Time of collapse, sec.	88	108	108	22	6

a poorly marked maximum (20 sec) in 0.016*M* solution[19]. The time of collapse of *p*-cresol foams was independent of concentration (22–26 sec) between 0.003 and 0.05*M* but reached 32 sec in 0.18*M* solution.

The cresols are ionized in aqueous solutions, and their foaminess depends on acidity or alkalinity[18]. Hydrochloric acid accelerated the collapse of foams after shaking. The effect of sodium hydroxide is illustrated in Table 5. It is seen that small additions of alkali raise and large additions depress the foaming capacity.

Qualitative observations on foam stability of 0.05 per cent solutions

of chlorinated phenols have been published by Haefele[24]. "Stable foams" were obtained with pentachlorophenol between pH 1.5 and 5 and between 8 and 9.5, for 2,4,5-trichlorophenol at pH 7 and 8, for 2,3,4,6-tetrachlorophenol at pH 9 and 10, etc.

Mixed aqueous solutions of glycerol and ethanol have been investigated by Nakagaki[23]. Fig. 19 shows the height (in cm) of the foam after a standard shaking. *W* is water, *G* is glycerol, and *E* is ethanol. The composition is by weight. The three maxima occurring in the system

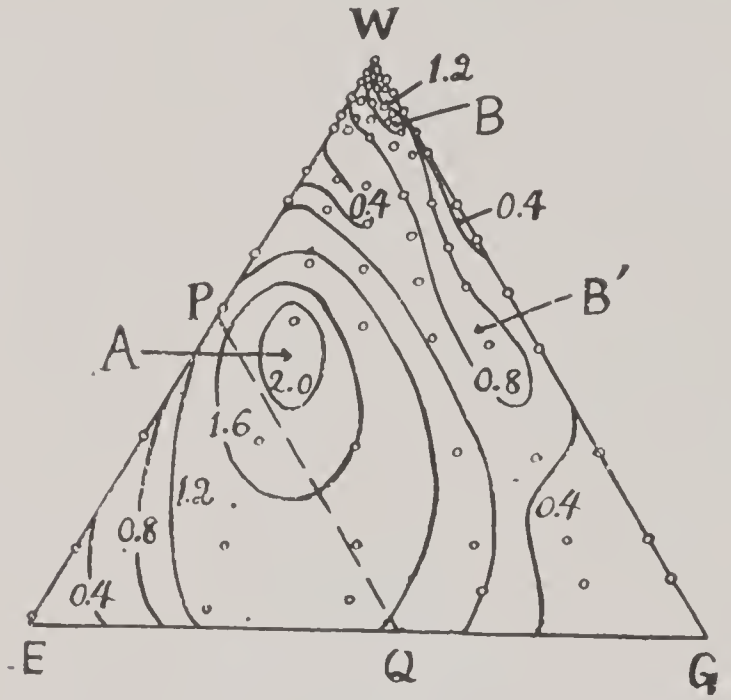


FIGURE 19. Foam height of water-ethanol-glycerol mixtures after a standard shaking. W = water, E = ethanol, G = glycerol. Figures: foam heights in cm. There are maxima at A, B, and B′. From *Bull. Chem. Soc. Japan*, **21**, 30 (1948).

are shown by letters, *A*, *B* and *B′*. *PQ* is the line corresponding to 45 per cent ethanol; it is drawn on this and the two following figures to facilitate the comparison of the compositions of the maxima *A*. Fig. 20 represents the time t_1 sec (see above, this section), and Fig. 21 the time t_2 sec in the same ternary system. All three figures are similar in the ethanol-rich region, but in the mixtures containing little ethanol there is more similarity between foam height and t_1 than between t_1 and t_2.

Section 36. *Aqueous solutions of fatty acids.* The foaminess of aqueous solutions of fatty acids varies with concentration in a manner

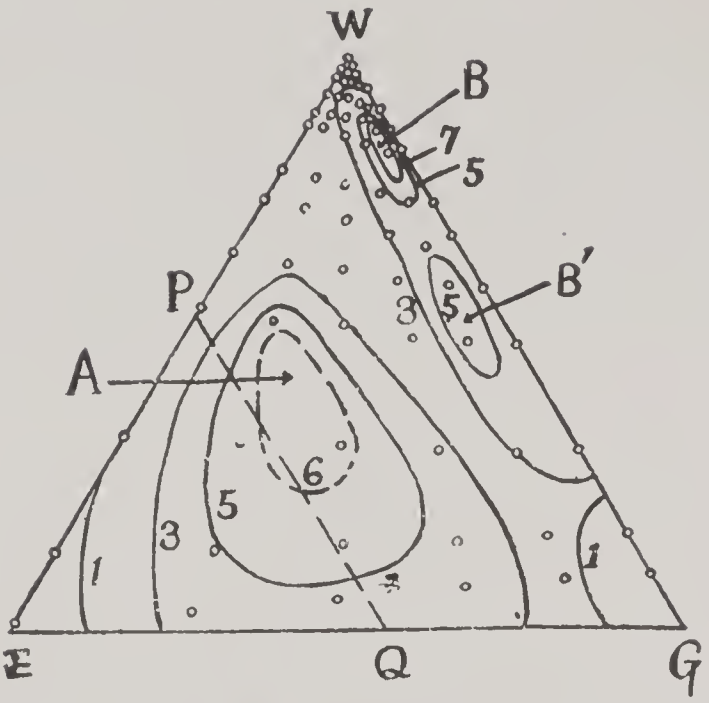


FIGURE 20. The time until liquid surface appears in foams (produced by shaking) of water-ethanol-glycerol mixtures. See Figure 19.

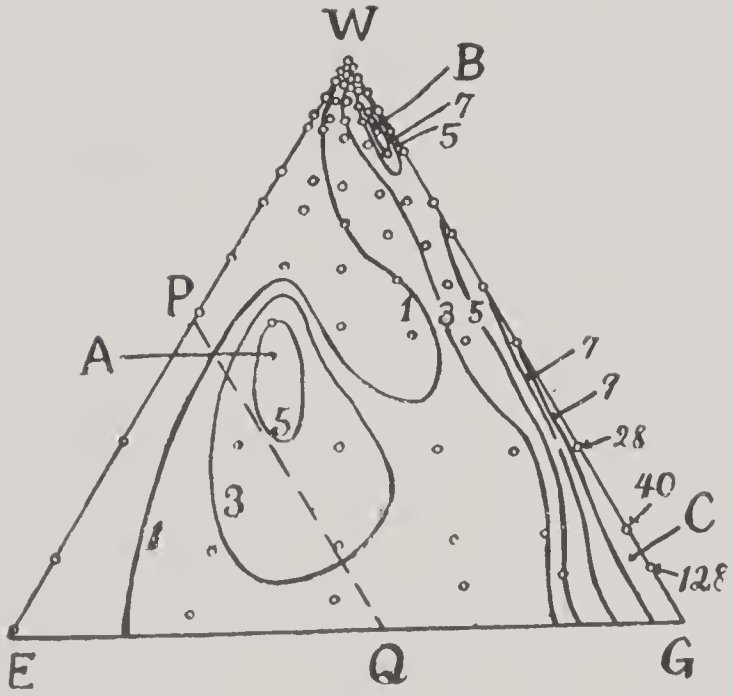


FIGURE 21. The time between the appearance of liquid surface and the collapse of the last bubble in foams (produced by shaking) of water-ethanol-glycerol mixtures. There are maxima at A, B, and C. See Figure 19.

similar to that of alcohols (see section 34). Table 6 summarizes the longest persistences in each system studied and the concentrations at which these maxima were observed.

The dependence of the maximum lifetimes on molecular weight is less clearly marked than in the alcohol series, but the tendency of the corresponding concentrations to decrease when the molecular weight increases is unmistakable. When considering these conclusions and generally the values listed in Table 6, it should be remembered that the foaminess of acids is likely to be sensitive to the

Table 6. Maximum Persistence of Foam of Aqueous Solutions of Fatty Acids and the Concentration Corresponding to This Maximum

Acid	Time of Collapse after Shaking	Ref.	Pneumatic h/u	Ref.
Formic	4 sec; 2.1 % w/v	14	2.9 sec; 5.8 % w/v	15
			14.7 sec; 8.75 % w/w	12
Acetic	11 sec; 15 % v/v	25	3.4 sec; 4.9 % w/v	15
	8 sec; 1.2 % w/v	14	21.8 sec; 2.5 % w/w	12
Propionic	11 sec; 1.9 % w/v	14	26.4 sec; 3.5 % w/w	12
Butyric	18 sec; 8.8 % w/v	14	31.2 sec; 2.5 % w/w	12
Valeric	9 sec; 0.15 % w/v	14	29.7 sec; 1 % w/w	12
Hexanoic	13 sec; 0.087 % w/v	14	37.0 sec; 0.035% w/w	12
			Single Bubbles	
Heptanoic	16 sec; 0.019 % w/v	14	19 sec; 0.18 % w/w*	3
	85 sec; 0.11 % w/w	26		
Octanoic	12 sec; 0.0036% w/v	14	23 sec; 0.05 % w/w*	3
Nonanoic	5 sec; 0.0010% w/v	14		

* These concentrations are calculated assuming the solubilities of heptanoic and octanoic acids to be 0.22% and 0.062% respectively.

cations present in water and that some inconsistencies of the table may be due to differences between the water specimens used. The precision of the experiments does not seem to warrant a comparison between the persistences of alcohols and acids.

Lactic acid[14] had a maximum of the time of collapse (7.5 sec) in 1.0*M* solution.

For the foaminess due to unimolecular films of higher fatty acids, see section 41. For the foaminess of soaps, see section 38.

Fig. 22 illustrates the concentration dependence of the lifetime of single bubbles (apparently of approximately 0.15 cm in diameter) on solutions of heptanoic (enanthic) and octanoic (caprylic) acids[3]. The concentration is expressed as fraction of saturation (see Table 6, footnote).

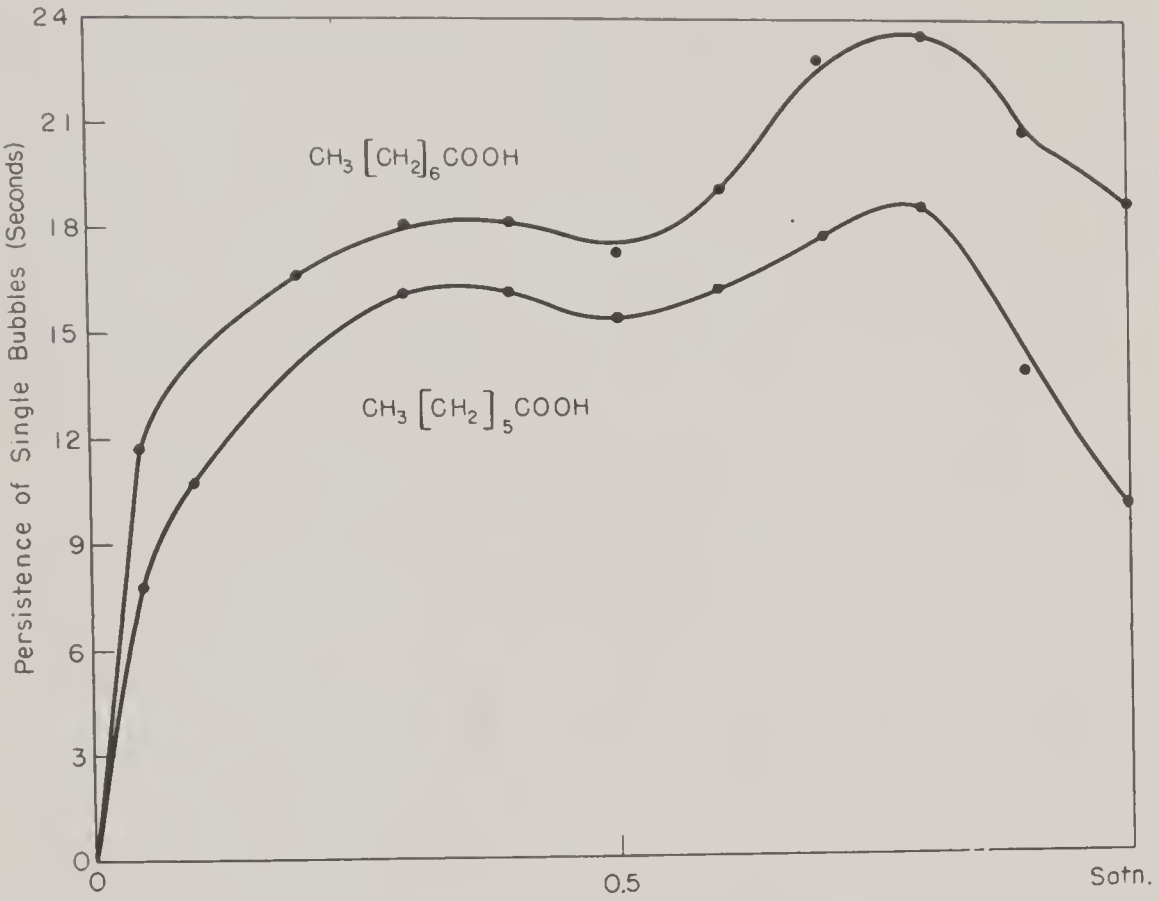


FIGURE 22. Lifetime of single bubbles in the surface of aqueous solutions of octanoic (upper curve) and heptanoic (lower curve) acids as a function of concentration. Data of Talmud and Sukhovolskaya[3].

Section 37. *Aqueous solutions of miscellaneous organic substances.* Maxima of the time of collapse after shaking and of the lifetime of single bubbles (marked by an asterisk) have been determined for the following systems:

Sucrose[14]	0.5*M* solution,	0.5 sec
Acetone[14]	0.5*M*,	2.5 sec
2-Pentanone[14]	0.05*M*,	3 sec
Acetaldoxime[14]	0.37*M*,	10 sec
Paraldehyde[14]	0.03*M*,	9 sec
Ethyl acetate[14]	0.01*M*,	2.5 sec
Nitrobenzene[14]	0.005*M*,	6 sec
Ethylamine[14]	0.4*M*,	12 sec
Aniline[14]	0.1*M*,	11 sec;
	0.24*M*,	19 sec (*, ref. 3)
p-Toluidine[14]	0.04*M*,	6 sec
α-Naphthylamine[18]	0.0017*M*,	18 sec

Some data for the time of collapse after bubbling air through solutions of *p*-toluidine, methylaniline, and dimethylaniline can be found in ref. 19. The time of collapse after shaking 0.0003 and 0.0006 per cent solutions of methyl salicylate was 2 and 1 sec, respectively[27].

Section 38. *Aqueous solutions of soaps.* Aqueous solutions of the sodium salts of the fatty acids containing less than 12 carbon atoms do not give the typical stable lather of the soaps having a longer chain (see, e.g., ref. 28). The foam persistence of the latter soaps is such that the methods best suited for evanescent foams (see sections 34–37) would be too time-consuming. The two methods used by Plateau, namely, observations on single films and single bubbles, seem most promising although they also may involve an inconveniently long waiting; some soap films in closed vessels have been kept for months (see section 39). Plateau's methods were applied by him to solutions of commercial soaps (usually containing also glycerol) but they have been little employed for studying individual salts.

A 3.7 per cent sodium laurate solution, pH 8.6, gave films which persisted for 120 to 400 sec when the diameter was 1.0 cm and for 13 to 32 sec when the diameter was 3.5 cm[29]. The most persistent bubble among an indefinite number of these (see section 19) produced on the surface of a 0.1 per cent sodium laurate solution, pH 7.6, had the lifetime of 61 sec; at pH 8.6 the greatest lifetime was 150 sec[28].

Fig. 23 shows the effect of concentration of sodium laurate on the foaming capacity determined in three different ways[30]. It is seen from curve 1 that the persistence of single bubbles, whose diameter was about 1 cm, had a maximum (about 350 sec) in 0.02N solution (i.e., 0.44 per cent). The time (curve 2) for the foam produced by pouring to subside to one-half the original volume also exhibited a maximum (whose absolute value was much greater than the average persistence of a single bubble), but at a higher concentration. However the original volume of foam produced by pouring (see section 25) was almost constant between 0.01 and 0.06N concentrations (curve 3).

The sodium laurate solutions used by Burcik manifested a shallow minimum of surface tension γ near the concentration of maximum persistence. It should be mentioned that low γ may cause too high results in the measurement of the persistence of single bubbles. When the same orifice is used for different solutions, the diameter of the bubble issuing from it is smaller the smaller γ (see section 3). When the

diameter of a bubble is less, its persistence increases (see section 19). Hence, at a constant orifice and a constant "true" stability, the measured lifetime is likely to be greater at small γ. However this effect alone would not account for Burcik's results.

The insensitiveness of the initial volume of foam produced by pouring to concentration changes follows also from the earlier work by Miles

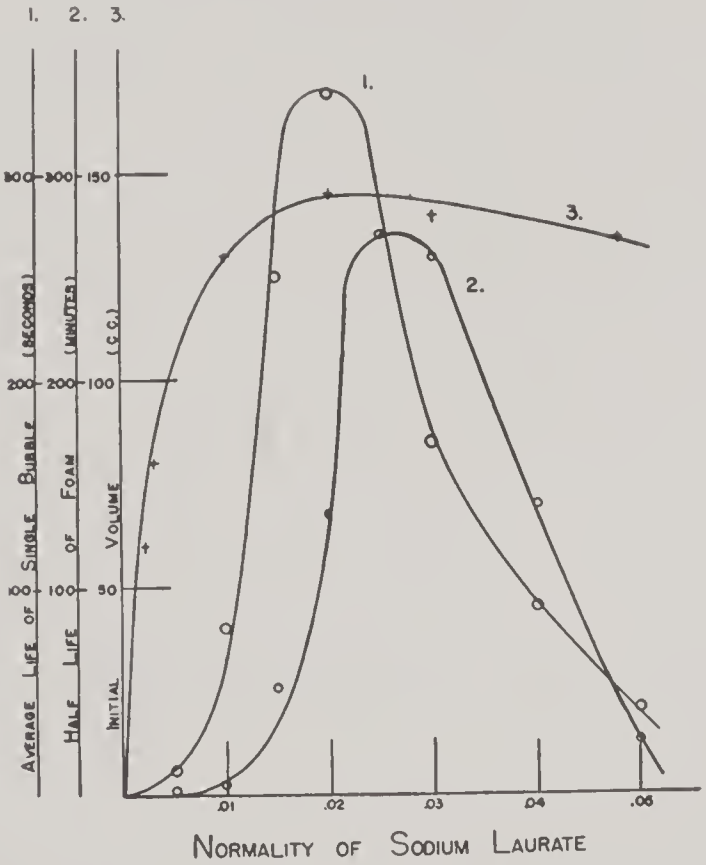


FIGURE 23. Stability of sodium laurate foams as a function of concentration. 20.0°C. From *J. Colloid Sci.*, **5**, 421 (1950).

and Ross[31]. There was an increase of only about 10 per cent in this volume when the concentration of sodium myristate or sodium oleate increased from 0.1 to 0.4 per cent. (In these experiments the pH of each solution was adjusted to give the greatest possible foam volume.) Perhaps, when the lifetime of foam films is long, the initial volume of foam in "pour test" is determined by the ease of incorporating gas in liquid, i.e., a process not directly connected with foaming capacity (see section 26).

When foam is formed by up-and-down movement of a perforated plate (section 25) its volume increases with the soap concentration but the increase is small at higher concentrations[32]. Thus the foam

volumes of 0.1 and 0.4 per cent sodium palmitate solutions were in the ratio 29:30, and the same ratio was observed for sodium oleate. Presumably in this instance again the volume of air which can be incorporated limits the foam volume. The time of collapse (t_3) to one-half the initial volume generally increased with concentration but there were also exceptions. Thus the initial foam volume of 0.8 per cent sodium palmitate was by 5 per cent greater than that of 0.2 per cent sodium palmitate, but its t_3 was 10 min. as against 50 min. for the 0.2 per cent solution.

The volume of foam made by shaking in a separatory funnel had a maximum value at some medium concentration of potassium oleate, sodium oleate, potassium laurate, and potassium myristate[33].

Fig. 24 represents the height of foam, produced by pouring, of 0.1 per cent soap solutions at 57° and different pH values[31]. The pH of the most voluminous foam increased from sodium decanoate to sodium palmitate. A change by two pH units was sufficient to lower or to increase the foam height severalfold. Evidently the foaming capacity of free fatty acids and "acid soaps" is small compared to that of "neutral soaps."

Fig. 24 refers to a temperature high enough to have the soap in solution. 0.1 per cent solutions of sodium myristate and sodium palmitate contain, at 25°, fine precipitate which seems to stabilize the foam. The most persistent bubble on these solutions had a lifetime of about 150 sec[28].

The increase of foam height with molecular weight seen in Fig. 24 is not always observed. In Götte's experiments[32] palmitate solutions gave more copious foams than stearate solutions of the same weight concentration. The temperature was 60°, and presumably both salts were truly dissolved. The time t_3 increased with molecular weight; e.g., for 0.4 per cent solutions, it was 20 sec for sodium decanoate, 10 min. for sodium laurate, 30 min. for palmitate, and 50 min. for stearate.

Sodium oleate gave more voluminous foam than sodium stearate but its t_3 was smaller (15 sec for 0.4 per cent solution)[32]. In 0.1 per cent solutions, sodium undecylenate yielded a foam height of 3 cm and sodium oleate one of 25 cm, and in 0.4 per cent solutions the values were 16 cm and 27 cm, respectively, all at 57° and the most favorable pH[31]. An increase in foaminess with the concentration of sodium oleate (between 0.001 and 0.01*M* solutions) was observed also by means of the pneumatic method[34]. At pH 7.5 sodium oleate

bubbles lasted up to 49 sec in 0.1 per cent solution[28]. A much greater (average!) persistence was observed earlier[17], namely, 23 and 4.5 min. for 0.1 cm and 0.45 cm large bubbles on a 0.15 per cent (0.005*M*) solution. The difference presumably is due to the different conditions

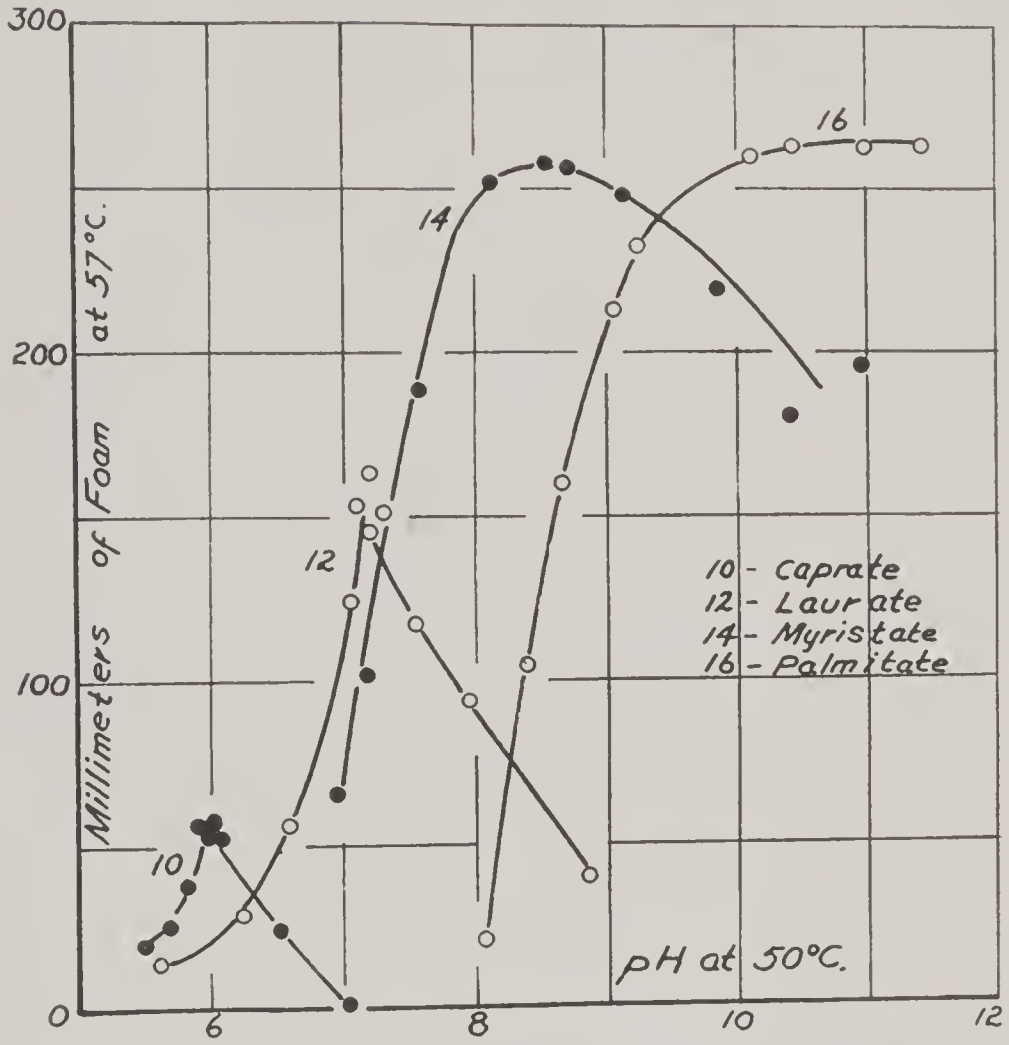


FIGURE 24. Foam heights (after pouring) of 0.10% solutions of sodium salts of saturated fatty acids as a function of pH at 57°C. From *J. Phys. Chem.*, **48**, 280 (1944).

of evaporation: in the experiments by Merrill and Moffett a current of dry air passed over the surface covered by the bubbles. Johlin[35] determined the stability of sodium oleate foams by a method not specified and found that it was maximal in 0.0019*N* solution at which concentration his sample showed also minimum of surface tension.

Some values for sodium linoleate and sodium ricinoleate can be found in ref. 28, values for sodium ricinoleate and sodium elaidate in ref. 31, and those for sodium ricinoleate in ref. 34.

Mixtures of two soaps (sodium laurate and sodium palmitate) may give a greater foam volume in a "pour test" than each of the pure soaps alone[31]. Because of the great sensitivity of the foaminess of soap to the acidity of the solution, the second soap may affect the foam volume because of its effect on the pH rather than because of its particular molecular properties[35a]. Thus 0.1 per cent sodium oleate solutions had greatest foam volume (after shaking) when their pH was confined between 9 and 10; at pH 7.5 this volume was negligibly small. When one part of commercial sodium ricinoleate was added to one part of sodium oleate (experimentally, 5 cm^3 of 2 per cent ricinoleate of pH 6.7 were mixed with 100 cm^3 of 0.1 per cent oleate), the volume and duration of foam decreased by about one-half, and pH was lowered from 8.3 to 7.7. If the ricinoleate solution was first made alkaline (to pH 8.4) and then mixed with the oleate solution, there was no depression of foaming capacity. Commercial sodium abietate did not affect either the pH or the foaminess of the oleate solutions[35a]. On the other hand, rosin (i.e., mainly abietic acid) was found to depress the foam volume of tallow soaps[35b]. See also section 43.

Addition of calcium laurate, myristate, or palmitate to a solution of sodium laurate, myristate, or palmitate did not greatly affect the foam volume of the latter[31]. Suspensions of calcium soaps do not froth appreciably; the utilization of this effect for titrating hard water is discussed in Chapter 14. The lifetime of the most persistent bubble in 0.1 per cent sodium oleate solution was greatly increased by salts such as NaCl and K_2SO_4, but the increase caused by some salts of alkaline reaction (0.01*M* K_3PO_4 or $K_4P_2O_7$) was even greater[28]. More complicated mixtures (soaps and "builders" in hard water) have been studied by Morrisroe and Newhall[36] and Dedrick and Wills[37] (see also section 46).

Trimethylvinylammonium palmitate gave rise to foam which was stable for weeks[38]. The volume of foam produced by shaking 0.14 per cent solutions of triethanolamine soaps increased from hexanoate to laurate and then decreased to stearate; and the oleate was almost as efficient as the laurate[39].

Section 39. *Solutions for stable films.* Soap gave name to soap bubbles, and a soap still is a usual constituent of solutions recommended for producing particularly persistent foam lamellae or bub-

bles. Plateau[40] used solutions of commercial soap in aqueous glycerol. (He had difficulties in procuring colorless and odorless glycerol samples.) Vegetable gums (gum karaya, gum tragacanth) can be used instead of glycerol to enhance the stability of soap films[28]. Dewar[41] employed aqueous solutions of 0.1 per cent ammonium oleate and 1 per cent glycerol as well as solutions of triethylamine, tetramethylammonium, and tetraethylammonium oleates.

In more recent time the following directions were tested with good results:

1. Dissolve 30 g castile soap in 1 liter distilled water without heating. After 24 hours of sedimentation syphon off the clear part and add to it ¾ of its volume of glycerol. Immediately before using add 0.025 to 0.1 g tannin to each 25 cm^3 of the solution[42].

2. Stir 10.5 g triethanolamine with 19.5 g oleic acid and let the mixture react for 24 hours. Dissolve it in 1 liter distilled water (no heating). Let settle for 24 hours. Syphon off the lower layer and mix 4 volumes of it with 3 volumes of glycerol[42].

3. Mix 15.2 cm^3 oleic acid with 73 cm^3 of 10 per cent triethanolamine solution, fill with distilled water to 200 cm^3 and add 164 g glycerol. Use the clear bottom layer[43].

4. Shake 2 g sodium dioctyl sulfosuccinate (sold as "Aerosol OT") with 98 g distilled water. Dissolve (gentle warming) 20 g sucrose and 13.5 cm^3 glycerol in 25 cm^3 of the above mixture[44].

Section 40. *Aqueous solutions of synthetic detergents.* Sodium alkyl sulfates, $NaO \cdot SO_2 \cdot O \cdot$alkyl, have been studied more than the other detergents. The persistence of single bubbles, about 1 cm across, of sodium dodecyl sulfate solutions had a maximum (90 sec) in 0.01N concentration[30]. According to Pankhurst[34] who employed a variation of the pneumatic method (section 21), noticeable foam formation at 38° is observed in solutions of sodium octyl sulfate at concentrations above 0.03M, while this minimum concentration of foaming is 0.02M for sodium decyl sulfate, 0.004M for sodium dodecyl sulfate, and 0.00025M for sodium tetradecyl sulfate; thus the threshold concentration decreased in the ratio 1 : 120 when the chain of the alkyl increased by 6 CH_2. When the concentration of the salt increased, foaminess passed through a maximum. This occurred in 0.02M solution of sodium dodecyl sulfate (i.e., at a higher concentration than found by Burcik) and in 0.002M solution of sodium tetradecyl sulfate. The

foaminess of dodecyl was greater than that of tetradecyl compound. The data are not sufficient for calculating h/u.

Maxima on the foaminess-concentration curve are observed also when the foam volume after shaking is taken as the measure of foaminess[45]. Thus, at 20° and 40°, 0.06M solution of sodium dodecyl sulfate gave more copious foam than either more or less concentrated solutions. The maximum for sodium tetradecyl sulfate was at 0.07M at 40° and 60° and at 0.04M at 20°. At 60° the foam volume of the C_{12}

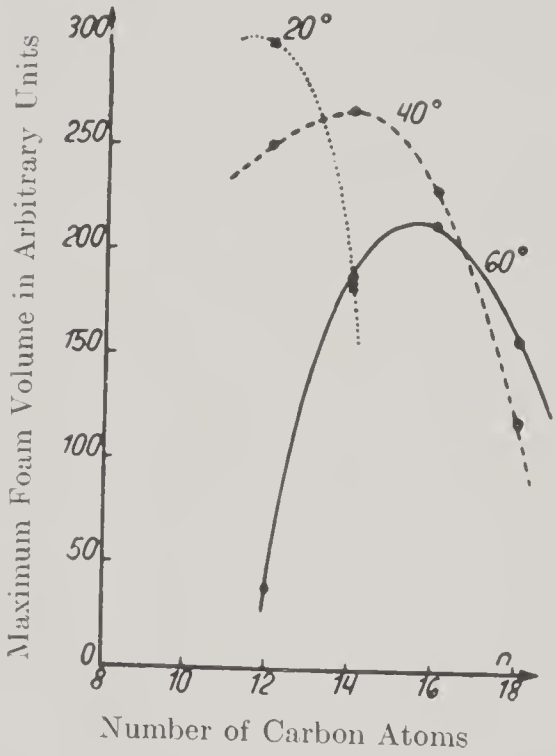


FIGURE 25. The maximum foam volume (after shaking) of sodium alkyl sulfate solutions. The three curves refer to 20, 40, and 60°C. From *Kolloid-Z.*, **64**, 327 (1933).

compound was almost independent of concentration between 0.01 and 0.1M. Sodium hexadecyl and octadecyl sulfates showed no maximum within this concentration range at 40°, but at 60° the maxima were situated near 0.03M and 0.005M, respectively. The foam volumes (in arbitrary units) corresponding to these maxima are plotted in Fig. 25 along the ordinate. The number of carbon atoms in the sulfate molecule is plotted along the abscissa. The three curves belong to the three temperatures marked on the graph. It is seen that the foam volume of the C_{12} compound is greater the lower the temperature while that of the C_{18} salt is at 60° greater than at 40°.

The foam volume produced by a moving perforated plate (section

25) increased with concentration although the increase was very slight at higher concentrations. For example, 0.1, 0.2, 0.4, and 0.8 per cent (i.e., 0.0035M, 0.007M, 0.014M, and 0.028M) solutions of sodium dodecyl sulfate had volumes in the ratios 0.64:1:1.18:1.22. The time t_3 (see section 38) had a maximum (20 sec) in 0.1 per cent solution, i.e., at a greater dilution than the lifetime maximum of single bubbles. The foam volume little depended on chain length of the sulfate in relatively concentrated solutions; for example, it differed by less than 2 per cent for 0.4 per cent solutions of the C_{12}, C_{13}, C_{14}, C_{16}, and C_{17} sulfates and also of the unsaturated sulfate having the oleic acid chain. However, in lower concentrations (e.g., 0.016 per cent) shorter ions (C_{12}) gave less foam and had smaller t_3 values than longer ions (C_{16} or C_{17}). Sodium octadecyl sulfate was in all respects a poorer frother than the next lower homolog[32].

Miles and Ross[31] and Dreger *et al.*[46] applied the "pour test" (section 25) to many sodium alkyl sulfates. The foam height H first increased with concentration and then reached a value independent of concentration and almost independent of the salt used. Also in this instance (see section 38) perhaps the volume of air incorporated into the liquid during the impact was measured rather than any property of the foam films. The concentration C_1 at which the constant value of H was attained depended on the nature of the solute. At 46° it was about 0.005M for sodium dodecyl sulfate, about 0.003M for sodium tetradecyl sulfate, and about 0.001M for sodium cetyl sulfate. A similar dependence of C_1 on the chain length was observed also for sodium sulfates of 2-hendecanol, 2-tridecanol, 2-pentadecanol, 2-heptadecanol, and 2-nonadecanol. There was no definite difference between the sodium sulfates of 2-pentadecanol and 4-pentadecanol, but 6-pentadecanol and 8-pentadecanol had greater C_1 and also a greater limiting height H than the first named isomer.

Change of pH between 3 and 9 had but little effect on the H of 0.1 per cent (i.e., 0.0035M) solution of sodium dodecyl sulfate[31]. Large excess of neutral salts (sodium chloride, magnesium chloride, calcium chloride) and of hydrochloric acid greatly increased the H of 0.0023M sodium sulfate of 7-tridecanol; e.g., in 0.5N hydrochloric acid, H was 10 times as great as in distilled water[46].

Some sodium alkyl sulfates, within a range of ratios, are incompatible with soaps. Thus the time of collapse (after shaking) of 0.25 per cent solution of the sodium 6- or 7-tetradecyl sulfates was lowered from 15 min. to a few seconds by addition of 1 part of sodium stearate

to 200 parts sulfate. Smaller and greater ratios of stearate to sulfate were less deleterious[47]. The effect of calcium salts on the foaminess of mixtures of sodium tetradecyl sulfate and soap also has been studied[31].

Long-chain alkyl sulfuric acids are suitable frothers in flotation. They froth in alkaline, neutral, and acid solutions. They share this property with long-chain esters of betaine chloride [$(CH_3)_3$-$NCl \cdot CH_2COO \cdot$alkyl], compounds of the type $CH_3[CH_2]_9\ CH_2$-$CO \cdot O \cdot [CH_2]_2 \cdot O \cdot [CH_2]_2 \cdot O \cdot SO \cdot ONH_4$, and so on[48]. Sabetay[49] was impressed by the ability of the lauric acid ester of triethanolamine [$C_{11}H_{23} \cdot CO \cdot O \cdot CH_2CH_2N(CH_2CH_2OH)_2$] to foam in relatively concentrated hydrochloric acid.

Data for the time of collapse of the froth of sodium dioctyl sulfosuccinate and sodium 6-butylnaphthalene-1-sulfonate under various external conditions have been published by Savitskaya and Rebinder[50]. Time t_1 (see section 29) was prolonged by adding agar to the detergent solution, particularly if the collapse occurred in closed space. Thus it was about 2 hours for 0.125 per cent sodium dioctyl sulfosuccinate and about 15 hours for this solution plus 0.1 per cent agar, both under an inverted beaker (see section 30). A 0.015 per cent solution of this detergent did not give any appreciable foam. Small additions of agar did not change this behavior, but when the agar concentration exceeded 0.08 per cent, t_1 measured in hours was observed. Thus two solutes, each of which caused no frothing, produced a strongly foaming liquid when combined[50]. Soap readily destroys foam of sodium dioctyl sulfosuccinate[47].

Sodium salts of aliphatic sulfonic acids (alkyl$\cdot SO_2 \cdot ONa$) are, as frothers, almost as efficient as sodium alkyl sulfates[32]. For example, in 0.1 per cent solution the tetradecane sulfonate gave foam volume of 54 (arbitrary units) and t_3 (section 38) of 8 min., while the tetradecyl sulfate had volume of 57 and t_3 of 11 min. Sodium cetanesulfonate was a poorer frother than sodium tetradecanesulfonate or sodium cetyl sulfate.

Solutions of sodium β-lauroylamino-ethanesulfonate, $C_{11}H_{23}$-$CONHCH_2CH_2SO_3Na$, are said to be better frothers than the homologous compounds derived from decanoic, myristic, palmitic, or stearic acid[50a].

The foam height (after shaking) of mixtures of commercial soap with several commercial sulfonates (such as sodium dodecylbenzenesulfonate) was determined at 30° and 60° by Reutenauer *et al.*[51].

Disodium α-tocopheryl phosphate (a salt of vitamin E) is not a

commercial detergent but has very similar physical properties. A 0.43 per cent solution of its monohydrate gave films which lasted for 30 to 39 sec (averages of ten) when the film diameter was 3.5 cm and for about 7 min. when the diameter was 1.0 cm[29].

The foam height (after pouring) of some nonionic detergents of undisclosed composition had a maximum in 2 or 4 per cent solutions[52].

Alcohols ROH were condensed (at 150° in a nitrogen atmosphere in the presence of 30 per cent sodium hydroxide) with approximately 1, 3, or 6 parts by weight of ethylene oxide, and the products (apparently not further purified) were dissolved in water and subjected to a "pour test" (see section 25). The foam height usually increased with concentration. Thus for R = decyl and 3 parts of ethylene oxide, this height at 50° was 98 in 0.05 per cent and 198 in 0.5 per cent solution. At 0.5 per cent concentration, it was greater the shorter the radical R (from decyl to cetyl). Condensation with 3 or 6 parts ethylene oxide yielded better frothers than that with one part. The height of foam 15 minutes after its formation was, for example, one-quarter of the original height[52a].

The height of foam produced by shaking aqueous solutions of commercial detergents is said to be greater the more "hydrophilic" the detergent[52b].

Section 41. *Unimolecular layers.* Gas bubbles under the surface of water have a comparatively long lifetime if the surface is covered with a "monolayer." When the bubble persistence τ is plotted against the surface concentration (expressed, for instance, as the number of molecules of the surface film on 1 cm^2), curves with a sharp maximum result[53]. Fig. 26 combines the results of Talmud and Sukhovolskaya[3] on 0.15 cm large bubbles under films of ethyl oleate on water, and those of Trapeznikov[54] on 0.3 cm large bubbles under ethyl palmitate on 0.01*N* hydrochloric acid. The ordinate is the average persistence (in sec) and the abscissa is the number of gram-molecules on cm^2. For surface concentrations less than 2.7×10^{-10} g-mol./cm^2 there are two curves for ethyl palmitate. The lower curve represents the average of all the bubbles observed (10–20) while for the upper curve the bubbles which broke at once were disregarded.

The maximum on the ethyl oleate curve corresponds to the area of 185 sq A per molecule, and the maxima on the ethyl palmitate curves to areas of 130 and 100 sq A. All these areas are much greater

than that of the "completed monolayer" which is, for example, 22 sq A for ethyl palmitate. According to Trapeznikov, the surface film at 2.7×10^{-10} g-mol./cm^2 (i.e., 61 sq A) is dense enough so that

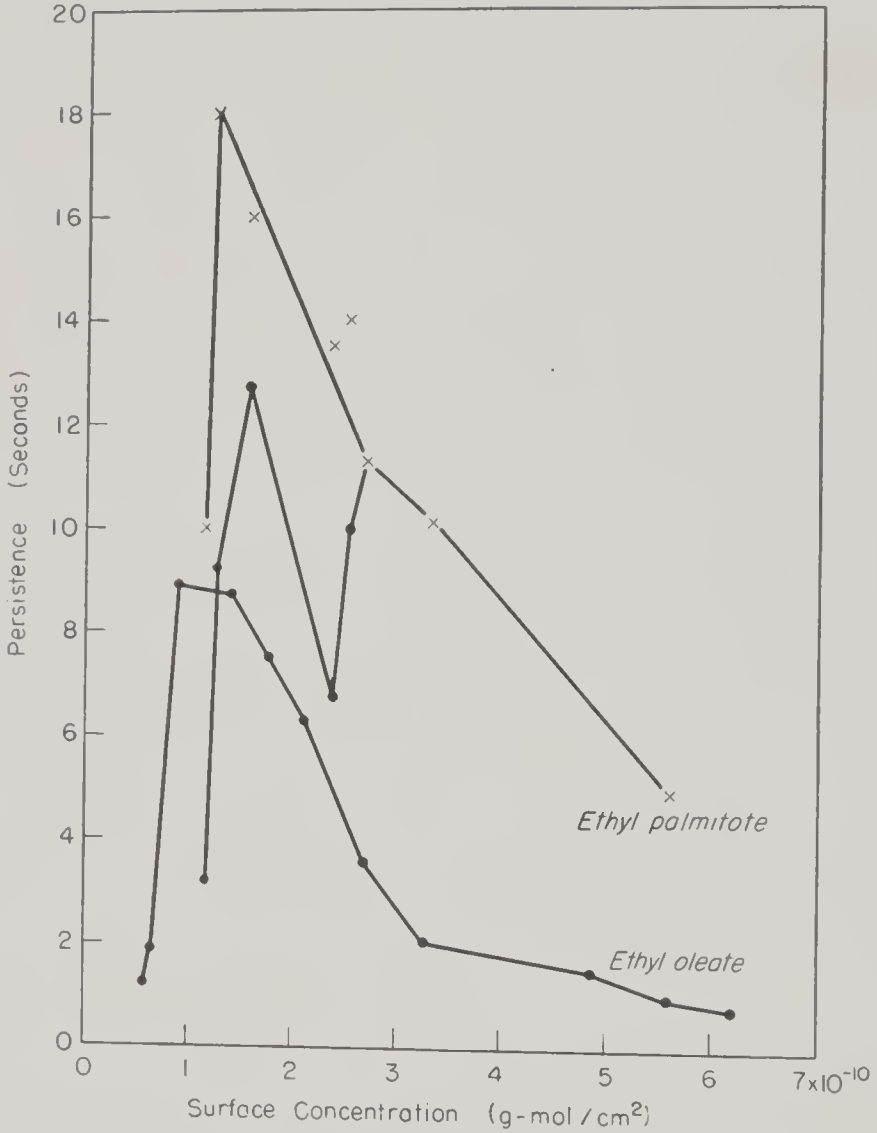


FIGURE 26. Persistence of single bubbles under unimolecular layers of esters as a function of surface concentration. Data of Talmud and Sukhovolskaya[3] and Trapeznikov[54].

every rising bubble is stopped by the monolayer; at larger surface areas many bubbles meet pure water surface on rising and burst immediately. This explains the advisability of plotting non-zero values of lifetime separately, as long as the surface concentration is less than 2.7×10^{-10}.

Two esters have been selected for Fig. 26 because ester films are less likely to be affected by ionic impurities in the water used; thus

Talmud and Sukhovolskaya observed different τ with different samples of distilled water except when the film was of ethyl oleate.

For cetyl alcohol the maximum of τ (2.3 sec) was at 6.4×10^{-10} g-mol./cm^2, i.e., 26 sq A/mol.^{3}. On 0.01N hydrochloric acid the following maxima of τ were found[54]: palmitic acid 6 sec, 24 sq A at 24°; myristic acid 6 sec, 43 sq A at 24°; lauric acid, no definite maximum, $\tau = 2$ sec between 60 and 160 sq A at 18°; cetyl alcohol 3 sec, 20 sq A at 18 to 20°; cetyl stearate 3 sec between 22 and 38 sq A at 22°. At a higher temperature (32°) the maximum of τ (10 sec) for palmitic acid on 0.01N hydrochloric acid shifted to 35 sq A. It is seen that the areas of the maximum τ either agree with those of a "completed monolayer" or are larger. In all instances compression of the monolayer to areas less than 20 sq A/molecule immediately reduced τ to zero. In Fig. 26 extrapolation of the curves to higher surface concentrations would lead us to expect $\tau = 0$ at about 8×10^{-10} g-mol./cm^2, i.e., at 21 sq A/molecule.

Isemura's work[55] on the persistence of bubbles stabilized by monolayers is known to the author from an abstract only.

The bubbles under unimolecular layers differ from all other bubbles in that their interior surfaces have a surface tension different from that of the exterior surface. Using the terms of section 14: the roof of the dome and the plane liquid-air interface around the bubble have surface tension γ_1 of the contaminated surface, while the ceiling and the floor of the bubble have the greater surface tension γ_0 of the pure solvent. Instead of the equation $2 \cos \alpha + \cos \beta = 1$, equation $\gamma_1(1 - \cos \alpha) = \gamma_0(\cos \alpha + \cos \beta)$ results. Bubbles under a monolayer should be less flat than equally large bubbles of the ordinary kind. No comparison of the shapes of the two types of bubble could be found in the literature. The conditions of stability of the bubbles under a monolayer apparently have never been properly discussed.

Section 42. *Foaminess, composition, and concentration.* A definite correlation between the composition of a substance and its ability to produce foam is very unlikely (see section 95). However, if only aqueous solutions about as viscous as water itself are considered and temperature differences may be neglected, it is legitimate to inquire how the stability of a foam is affected by variation of the chemical composition and structure of the solute.

Consideration of 114 frothers tested for flotation purposes showed

that efficient frothers contained (preferably one) hydroxyl, carboxyl, carbonyl, or ester group and a chain of at least six carbon atoms; their solubility should be of the order of 1 g/1. Frothers which at the same time were collectors (see Chapter 13) usually contained amino groups and had more than six carbon atoms[56]. These rules based on the experience of a particular industry cannot claim any general validity.

The "frothing power" (not further defined in the abstract) of aliphatic acids is said to be greater than that of the corresponding aldehydes which often are better frothers than the corresponding alcohols[57]. In the alcohol series, the "frothing power" increased with chain length to C_8. It was greater for normal than for branched alcohols and greater for aliphatic than for aromatic alcohols. Unfortunately the original paper was not accessible.

It appears from Tables 4 and 6 that foaming capacity rises to a maximum and then decreases when the molecular weight of the alcohol or the acid increases. The existence of these maxima may be due to solubility effects. The solubility of aliphatic alcohols and acids in water generally is smaller the greater the molecular weight. For substances containing more than six carbon atoms in the molecule the solubility may be so low that even the greatest concentration realizable is still too small for the foaming to be considerable. If solutions of homologous alcohols or acids are compared at a constant concentration, considerably smaller than the solubility of the least soluble member of the series, the "activity" of the frother (i.e., the foam persistence divided by concentration) is seen to increase with molecular weight also beyond hexanol and hexanoic acid.

According to Bartsch[14], Rebinder[20, 58], and others, concentrated solutions of higher alcohols and acids froth poorly because they contain microscopical or submicroscopical droplets of the nonaqueous phase. This, then, would be the reason for both the maximum of foaminess at a medium molecular weight and the maximum on the foaminess-concentration curve. Elimination of the droplets would remove these maxima. Rebinder filtered aqueous isoamyl alcohol solutions and cooled the filtrates to 5° (the solubility of isoamyl alcohol in water is greater at lower temperatures). Filtration alone and especially both treatments together depressed the maximum of the persistence τ of single bubbles (at room temperature); after the combined treatment the maximum practically disappeared and τ had a nearly constant value (75 sec) between 0.07 and 0.3 g-mol./1.

Also the striking difference between τ in open and closed vessels was greatly attenuated by the removal of the droplets; this was observed on 1-octanol solutions, and the droplets were removed by filtration. Unfortunately it is not stated what was the change in the over-all concentration produced by this treatment. Destruction of foam by emulsions has been noted many times (see section 51).

For another explanation of the maximum on the foaminess-concentration curve, see section 100.

In aqueous solutions of isoamyl alcohol the foaming capacity increases with concentration C when $C < C_m$ (C_m is the concentration corresponding to maximum persistence) and decreases when C increases past C_m. There is another difference between these two concentration ranges[10]. When an aqueous solution of methyl orange is mixed with isoamyl alcohol and shaken, the foam is colored when $C < C_m$, but the dye solution rapidly drains from the froth when $C > C_m$. When the oil-soluble dye Sudan IV is dissolved in isoamyl alcohol, diluted with water and shaken, the froth is pink at $C < C_m$ and white or greenish-white at $C > C_m$. No complete explanation for this behavior has been given so far.

Section 43. *Aqueous solutions of poorly identified organic substances.* Many determinations of foaminess have been carried out on systems so complicated that they do not throw any light on the relation between the structure and the frother activity of a substance.

Pine oil is used as frother in flotation. The volume of foam produced by the pneumatic method in various specimens of pine oil and in the main constituents of this oil (α- and β-terpineol) was compared with the foam volume of hexanol[58a]. Kerosene extended the time of collapse of foam produced by shaking an aqueous solution of pine oil; thus addition of 1 g/l of kerosene to 11 mg pine oil in one liter of water raised this time from 5.5 to 10.0 sec[58b].

Although different *saponins* have different foaming properties[59], many experimenters characterized their substances simply as "saponin." The stability of foam (produced apparently by the pneumatic method) was for saponin solutions greater than for peptone > gelatin > albumin > pectin > casein solutions[60]. In a modified pneumatic method there was apparently a maximum of persistence between the concentrations of 0.01 and 0.2 per cent. For the time of collapse after

shaking there was no difference between 0.5 and 1 per cent solutions (170 sec) but this time was only 160 sec in 0.25 per cent and 120 sec in 0.008 per cent solution[17]. Solutions containing only 0.00018 per cent saponin did not foam on shaking, but 0.0009 per cent solution gave a measurable although evanescent foam[61]. According to Schütz[62] the logarithm of foam persistence is a linear function of the saponin concentration.

Destruction of saponin foam by ethyl alcohol was known to Plateau[63]. Sasaki[61] reports that moderate additions of ethanol (e.g., 0.26 g-mol. to 0.009 g saponin in 1 liter water) increase the height of foam caused by shaking while too much ethanol (e.g., 1 g-mol.) reduces the time of collapse without sensibly affecting the initial foam height. Isoamyl alcohol increased the time of collapse divided by the initial foam height of a 0.0009 per cent saponin solution starting from $3 \times 10^{-5}M$, and the persistence showed a maximum at the addition of 3×10^{-4} g-mol. isoamyl alcohol to 1 liter[64]. The time of collapse of 0.008 per cent saponin foam was considerably shortened by $0.037M$ isoamyl alcohol[17], i.e., a concentration over 100 times as great as the just mentioned optimum concentration.

Addition of soap to saponin or of saponin to soap in aqueous solution decreases the foam volume[65]. There is a range of saponin-soap mixtures which gives no noticeable foam. Its extent depends on the nature of the saponin and the soap (the sodium salts of abietic and several fatty acids were tried out)[66]. The mutual quenching of soap and saponin foams appears remarkable. Whether saponin displaces soap or soap displaces saponin, the resulting solution still should froth copiously. The explanation of the riddle seems to have been found in the acidity of the usual saponins[67] (see also section 38). When saponin is added to a sodium oleate solution, "acid soap" and eventually oleic acid form. They displace both saponin and neutral soap from the surface but are themselves poor frothers (see Fig. 24, section 38). When 0.1 g saponin was introduced into solution of 0.1 g sodium oleate in 100 cm^3 water, the pH of the solution changed from 8.1 to 6.9 and the foam volume (after shaking) decreased from 525 cm^3 to zero. A saponin solution in caustic soda, aged until its pH was stable at 8.4, had no quenching effect on soap foam. In the absence of surface-active competitors, saponin foamed equally well between pH 6.2 and 9.6. The time of collapse was more sensitive to foreign substances than the foam height; thus it was at pH 9.6 one-ninth of that at pH 8.1, and 0.01 g saponin added to 0.1

g sodium oleate was sufficient to reduce the time of collapse to 1/50th of its value for pure soap.

Bile acids and their salts give rise to relatively stable foams. The height of foam remaining a definite time after shaking was determined for commercial sodium glycocholate and its mixtures with sodium hexanoate, sodium undecylenate, and other soaps[68]. Bader and Schütz[69] measured the maximum persistence of bubbles (section 19) of commercial sodium cholate and sodium tauroglycocholate and, by foam fractionation, showed that these preparations were very impure (see section 110).

Section 44. *Proteins* yield persistent foams used, for instance, as food and in fire fighting. The stability of these foams depends above all on the pH of the solution (and on the purity of the sample which too often has not been tested). A maximum of stability usually is observed near the isoelectric point of the protein.

Thus, for gelatin whose isoelectric point was between 4.75 and 5.0, Bogue[70] found the greatest foam height (presumably after shaking) to occur at pH 5; this height was almost constant between pH 5.5 and pH 9 and sharply decreased between pH 9 and pH 10. Three samples of photographic gelatin gave maxima of foaminess near pH 6, but another sample had foaminess varying with pH in a complicated manner; a modified pneumatic method was used[34]. Electrodialyzed gelatin in 0.05 per cent solution had a maximum of foam height (in a pneumatic method) near the isoelectric point (pH 4.8), but 0.5 per cent solution of the same gelatin showed a minimum of foam height at this pH[70a]. Suppression of foaming (modified pneumatic method) on addition of larger amounts of alkali took place also in other experiments[71]. Deaminated gelatin, containing 17.38 per cent N instead of the original 17.96 per cent, had isoelectric point at pH 4, and the greatest foam volume after shaking occurred also at this pH[72].

A 0.05 per cent solution of egg albumin whose isoelectric point was at pH 4.6–4.8 foamed most at pH 4[73]. The pneumatic method was employed but unfortunately the dimensions of the apparatus are not given, and thus calculation of h/u (see section 22) is impossible. Two minima of the foam volume were visible at pH 2 and between pH 8 and 10, and in strongly acid (pH about 0) and strongly alkaline solutions (pH 12) the foam volume was about as great as at

pH 4[73]. Also a 0.1 per cent solution foamed best (in a pneumatic method) at its isoelectric point.[70a]

The isoelectric point of salmine sulfate is at pH 12, i.e., in a very different range of acidities. The average lifetime of single bubbles in 0.5 per cent salmine sulfate solution and the foam volume (pneumatic) of 0.05 per cent solution had maxima at pH 10[73].

The foaminess of alpha soybean protein solutions was studied by the pneumatic method but expressed as v_l/m (see section 24). Fig.

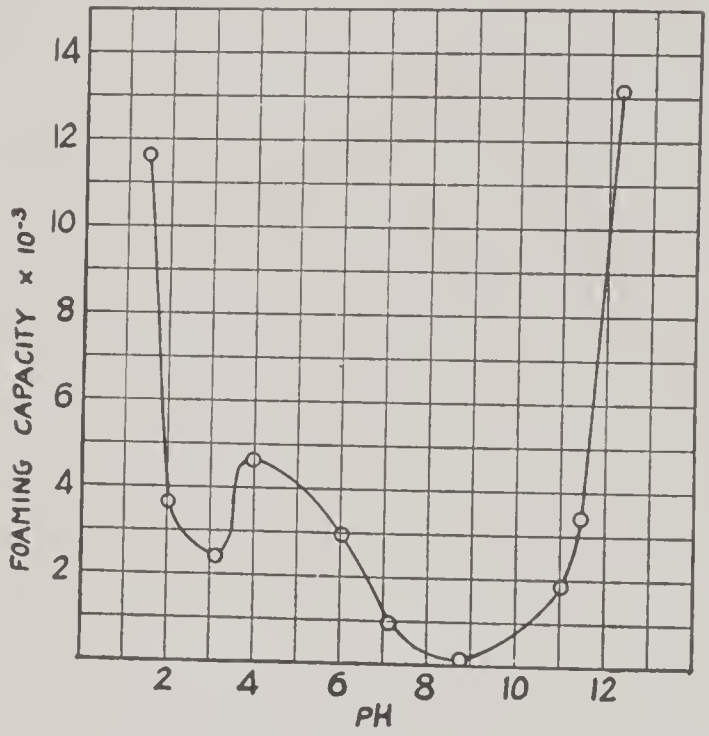


FIGURE 27. Effect of pH on "foaming capacity", i.e. volume of liquid in foam divided by the concentration of the solution (in special units), for alpha soybean protein in water. From *J. Phys. & Colloid. Chem.*, **51**, 661 (1947),

27 represents this magnitude as function of pH. As in the instance of egg albumen, there are a maximum near the isoelectric point (at pH 4.1), two minima in slightly acid and slightly alkaline solutions, and steep increases of foaminess in strongly acid and strongly alkaline media[74].

Salts affect the foaminess of protein solutions also when the pH is kept constant. Polyvalent cations may greatly increase the foaminess of proteins and their degradation products[75, 76]. Thus, v_l/m of an alpha soybean protein solution was 120 in water, 300 in 0.0001M sodium chloride, 1,600 in 0.0001M calcium chloride, and 2,900 in 0.0001M lanthanum chloride[74]. When compared in 0.1M concen-

tration, lanthanum chloride was not more active than sodium chloride, presumably because the charge on the protein particles was reversed by lanthanum ions. When 0.05 per cent egg albumen was dissolved in 0.001*M* potassium hydroxide to pH 10.5, the foam volume was about one-half that of a similar solution in 0.001*M* barium hydroxide at the same pH[73]. Sodium chloride lowered but calcium chloride raised the foam height (after shaking) of gelatin solutions[77].

Protein foams are destroyed or weakened by many additions. Albumin does not froth in an emulsion of water in benzene[78]. Stearic acid suppresses frothing of protein hydrolyzates[79]. Olive oil, oleic acid, sodium oleate, and calcium oleate lower the volume of foam produced by shaking animal glue solutions[80]. Milk fat and, particularly, oxidized fat reduce the foaming capacity of casein solutions[81]. The foaminess of protein mixtures was studied, e.g., by Trotman and Hackford[77] and by Pankhurst[34].

As mentioned in section 43, the foaming capacity of proteins is said to decrease from peptones to gelatin to albumin to casein[60]. Additional data on the foaminess of proteins refer, for example, to gelatin[82], albumin[83], and tannery proteins[84].

Solutions of *humic acid* at different acidities[85] and solutions of *gum arabic*[86] also have been studied.

Tannin in 0.2 per cent solution has a small time of collapse (t_1, see section 29) after shaking (a few seconds) but solutions of heptanoic acid in this tannin solution have very large t_1, e.g., 1500 sec as compared with 85 sec for the equally concentrated solution in pure water[26]. The increase of the stability of soap bubbles by very small amounts of tannin has been mentioned in section 39. Larger amounts quench soap foams; thus 0.02 g of tannin destroys the foaming capacity of 0.1 g sodium oleate in 100 cm^3 of water. Presumably tannin, which lowers the pH of the soap solution, acts in the same manner as saponin (see section 43).

The maximum persistence of air bubbles in solutions of *methyl celluloses* rapidly increased with the "molecular weight" (i.e., viscosity under standard conditions) of the sample[62]. The foaming of methylethylcellulose was reduced by sodium carboxymethylcellulose[87].

For the foaminess of various organic *dyes*, see refs. 17, 88, 89 and 90.

Section 45. *Solutions in organic liquids.* Solutions of hydrocarbons in hydrocarbons are capable of frothing. According to Bresler

and Talmud[91], concentrated solutions of diphenyl in benzene and of naphthalene in gasoline give foams as stable as those due to monomolecular films. Medicinal paraffin oils, which are supposed to consist of hydrocarbons only, gave the average lifetime of gas in the foam (L_g, see section 28) of 1 to 7 min. at 26° (the L_g of beer measured in similar conditions was 30 min.)[92]. The time of collapse (t) after shaking single hydrocarbons was less than 1 sec but mixtures of aromatic with aliphatic hydrocarbons had t as high as 6 sec (decane 2, butylbenzene 8 parts)[93]. Data are available for the foaminess of lubricants[92, 94, 22, 95], but it is unknown whether these were purely hydrocarbons.

A few solutions of nonhydrocarbons in hydrocarbons also have been studied. Single bubbles in 0.04N stearic acid in heptane lasted as long as 180 sec, presumably because the solvent evaporated and a solid film of the solute remained[17].

Single bubbles of air in the interface between n-hexane, n-octane, or nitrobenzene and the corresponding saturated vapors burst immediately as is usual with pure liquids[95a]. The persistence τ of bubbles in binary mixtures of these liquids showed maxima at 50 molecular per cents nitrobenzene + 50 molecular per cents hexane and 60 molecular per cents nitrobenzene + 40 molecular per cents octane (see also section 46). The effect of the atmosphere on the lifetime in the last named solution was studied. Under saturated vapor τ was, for example, 60 sec. When the gas phase originally contained only the vapor of the less volatile component (i.e., nitrobenzene), the lifetime was long (several hours). When the atmosphere contained octane only, the lifetime was approximately 15 sec. Ether vapor acted similarly to octane vapor[95a]. An explanation of this behavior can, perhaps, be given in terms of the Marangoni effect (see section 98). A foam film is stable if, on its expansion, the underlying solution having a greater surface tension is exposed. If the atmosphere contains such vapor and in such concentration that it can lower the surface tension of the new surface as soon as it is exposed, then the film has no "elasticity" and cannot last long.

Fig. 28 represents the time of collapse after shaking (section 29) homogeneous mixtures of methanol with hydrocarbons[96]. Curve 1 is for mesitylene, curve 2 for m-xylene, curve 3 for toluene, and curve 4 for benzene. The ordinate is the time (t) until but two bubbles remain, and along the abscissa the molecular per cents of methanol are plotted. The experiments were performed at 0°. The greatest t

for methanol-*p*-cymene mixtures was 142 sec, i.e., greater than for *m*-xylene and smaller than for mesitylene. In the system mesitylene-ethanol at 0°, the greatest t was 20 sec, and in the system *p*-cymene-

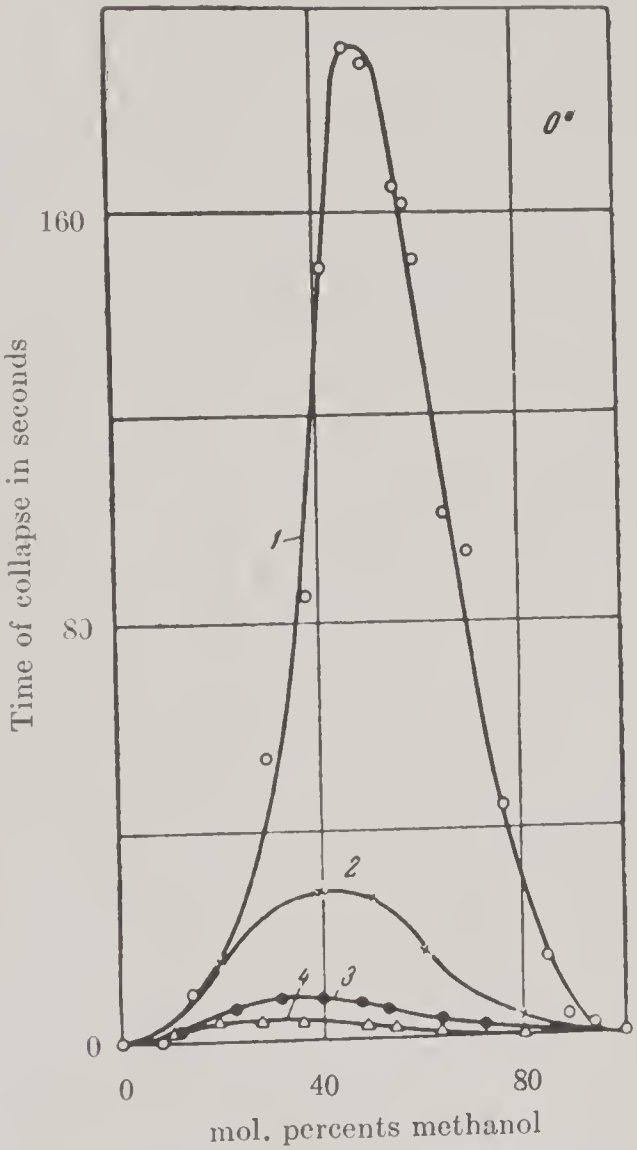


FIGURE 28. Time of collapse (until but two bubbles remain) of foams of mixtures of methanol with mesitylene (curve 1), *m*-xylene (curve 2), toluene (curve 3), and benzene (curve 4). From *Kolloid. Zhur.*, **12**, 378 (1950).

ethanol at 20° it was 6 sec. Mixtures of mesitylene and propyl alcohol gave a rather unstable foam; that is, stability decreased from methanol to propanol. Solutions of acetone or ether in mesitylene did not foam. Comparison of Fig. 28 with Fig. 17 and Fig. 22 indicates that the foaminess-concentration curves of solutions in hydrocarbons are generally similar to those in aqueous solution. However, the number of

solutes giving rise to froth in mesitylene seems to be less than the corresponding number in water.

A semiquantitative study of foam stability of solutions of commercial detergents in various organic liquids has been carried out by King[97]. The time of collapse after shaking was measured or estimated. The shortcomings of this method, especially when applied to very different liquids, are pointed out in section 29. In King's conditions, shaking produced no foam, for example, in glycerol solutions, and even a mechanical agitator yielded "merely emulsion of air bubbles." Relatively persistent foams were obtained with polyethylene glycols in methanol or acetone, and with sodium diamyl sulfosuccinate in benzene and other aromatic hydrocarbons, in nitrobenzene, and in other solvents.

Very stable foams can be produced in 2 per cent solution of sodium bis-(2-ethylhexyl) sulfosuccinate (presumably identical with the substance called otherwise sodium dioctyl sulfosuccinate) in triethanolamine[92]. The magnitude L_0 (see section 28) of this solution at 100° was 89 min.

A solution foaming at 200° was prepared[98] by dissolving 2 g of a soap (composition not given) in 1 liter of paraffin oil.

Every natural fat and oil contains several different substances. Nevertheless they are said to behave like pure compounds in that pure fats and oils foam poorly while their mixtures give relatively stable foams[99, 100]. Similarly to the presence of a frother in water revealing itself by the foaminess of the liquid, the presence of an "active" oil (e.g., linseed oil) in "inactive" oils (olive, peanut) can be detected from the enhanced foaming capacity of the sample[101]. The foaming of boiling butter is attributed to the presence of phosphatides[102]. Foaming of hot cottonseed and other oils was intensified by heating the oils in air (which presumably caused oxidation and polymerisation). This was demonstrated by keeping the oil for many hours at 190° and, from time to time, dropping "water-soaked pieces of bread" into it. The volume of foam generated by the steam was qualitatively estimated[103].

Section 46. *Foaming of ternary solutions.* In sections 34, 35, etc., examples have been given for the effects of a second solute (C) on the foaming of binary solutions containing solvent A and solute B. A third component of a solution can affect its properties in so many

ways that no definite rule governing the foam behavior of A + B + C as compared with that of A + B can be expected.

The change in foaminess caused by the addition of C is accounted for in an obvious manner when C chemically reacts with B. Thus calcium salts destroy the foam of sodium soaps (see section 38 and Chapter 14), since the calcium soap formed is not a frother. The effects of alkali on the frothing of *m*-cresol (see section 35) and the effect of pH on the frothing of solutions of proteins (see section 44), saponins (section 43), and soaps (section 38), belong to the same category.

The effect of an addition which does not chemically alter the first solute may, perhaps, be sifted into two groups observed, respectively, when C *is* (group *a*) and *is not* (group *b*) present in significant amounts in the surface layer.

Group a. Compound C may alter the degree of dispersity of B and thus affect its surface activity and "frothing activity". Nakagaki[90] pointed out that the series $NaNO_3 < NaCl < BaCl_2 < HCl$ was valid both for the rate of collapse of congo red foam after shaking and for coagulation of congo red sols. The efficacious electrolyte concentrations also were similar in both instances; for the most active electrolyte (HCl) the highest rate of collapse occurred in 0.0028*N* and the coagulation in 0.0043*N* solution.

Compound C may affect the surface activity of B by altering its solubility. Thus, the increase in foaminess of alpha soybean protein, caused by 0.5*M* sodium chloride and calcium chloride, is attributed to salting-out of the protein by the electrolytes[74]. The decrease in the time of collapse of aqueous alcohol foams caused by methanol may be due to better miscibility of ethanol with aqueous methanol than with water.

An analogous explanation was given for the effect of a third component on the foaming capacity of binary mixtures of nitrobenzene and cyclohexane[103a]. Some of these binary mixtures yield stable foams. Addition of piperidine lowers this stability although nitrobenzene-piperidine mixtures froth about as well as those of nitrobenzene with cyclohexane. Presumably, piperidine enhances the mutual solubility of cyclohexane and nitrobenzene. Ethyl alcohol has a smaller effect than piperidine. *p*-Cymene raises the foaminess of the above binary solutions, and in this ternary system the most stable foam is observed at 60 per cent nitrobenzene, 25 per cent cymene, and 15 per cent cyclohexane. *p*-Cymene and methanol are

miscible in all proportions but the complete miscibility is destroyed by adding small amounts of water (0.5 or 1 per cent) to methanol. In agreement with the above theory, mixtures of *p*-cymene and anhydrous methanol froth poorly, and foaminess is improved to a greater degree the more water is present (as long as the liquid remains homogeneous)[103b].

Compound C may affect the amount of B in the solution by displacing B adsorbed on some solid present in the system. This is the explanation given [103c] to the improvement of the efficiency of polyamides (as antifoaming agents in locomotive boilers) achieved by the addition of chestnut extract (100 parts for 0.2 part of polyamide and 1,000,000 parts water). Presumably, in the absence of the extract, polyamides are adsorbed by the sludge in the boiler.

Section 47. *Group b.* When C is present in the surface layer it may affect its properties without considerably displacing B, or it may displace B to such an extent that the properties of the surface are determined (almost) by C only.

Suppose that the surface layer of the binary solution contains emulsion droplets (see sections 42 and 51). Substance C present in this layer may cause dissolution of these droplets and, consequently, enhancement of foaminess. This is a possible explanation of the favorable effect of ethanol on the foam duration (time of collapse) of nonanoic acid and of isoamyl alcohol in water[14]. Benzyl alcohol lowered both the solubility of isoamyl alcohol and *m*-cresol in water and the time of collapse of their aqueous solutions; perhaps it gave rise to "two-dimensional emulsions."

The difference between the mechanical properties of surface layer consisting of B and those of a film of B and C is likely to be responsible for several observations. If, instead of monolayers of myristic or stearic acid or of cetyl alcohol, 1:1 mixtures of these substances with a hydrocarbon are deposited on water surface, the maximum of the bubble persistence τ (see section 41) disappears and τ becomes independent of film thickness (e.g., between 22 and 38 sq A./molecule)[104]. The stabilization of heptanoic acid froth by tannin and the mutual weakening of sodium stearate and sodium alkyl sulfate foams are mentioned in section 44 and section 40, respectively. In the experiments on saponin (section 43), small amounts of alcohol probably acted as plasticizer of saponin films, while greater amounts displaced

saponin and transformed the surface into one of aqueous alcohol which has a much shorter foam persistence than saponin surfaces. The favorable influence of glycerol on the lifetime of soap films is often attributed to the greater viscosity of the surface layers containing glycerol.

The displacement of a good frother by a poor frother from the surface layer is a well known phenomenon. It was postulated, for example, by Quincke[105] to account for the destruction of beer foam by ether vapor. (The foam of aqueous solutions of ether is short-lived.) Apparently it has never been proved by direct measurements of adsorption, but its existence is made nearly certain if it is found that the foam persistence of solution A + B + C is identical with that of A + C although the amount of B present may greatly exceed that of C. Thus the time of collapse t_1 (section 29) of $0.027M$ aqueous *m*-cresol solution was 25 sec and of $0.153M$ isoamyl alcohol solution 12 sec, while t_1 of the solution of 0.027 g-mol. *m*-cresol and 0.153 g-mol. isoamyl alcohol in liter was 11 sec, that is, nearly identical with t_1 of alcohol alone[18]. The relation between pH and the foaminess (by a modified pneumatic method) of a mixture of 0.5 per cent ovalbumin and 10 per cent gelatin was almost identical with that of 0.5 per cent ovalbumin alone[34].

As a condition of displacement, Quincke[106] assumed the validity of the relation

$$\gamma_{12} \leq \gamma_1 - \gamma_2 \tag{10}$$

In it γ_1 is surface tension of the binary solution A + B, γ_2 that of A + C, and γ_{12} is the tension along the boundary between the film consisting chiefly of C and the solution which contains almost no C. For example, when ether breaks beer foam, γ_1 is surface tension of beer, γ_2 is surface tension of beer whose surface is contaminated with ether, and γ_{12} is the interfacial tension between this ether-rich layer and the bulk of beer. Relation (10) is justified by the following reasoning. When the ether-contaminated surface increases by 1 cm^2, the surface energy increases by $\gamma_2 + \gamma_{12}$ ergs. At the same time the surface of pure beer contracts by 1 cm^2, and its surface energy decreases by γ_1 ergs. For the process to occur spontaneously, the decrease of energy must be at least equal to its increase. It is clear that, except for γ_1, the surface tension values are no equilibrium quantities. Rather, expression (10) has to be understood in this sense: when γ_2 and γ_{12}, which continually change because of the dissolution of ether in the

beer surface, reach values such that $\gamma_2 + \gamma_{12} < \gamma_1$ at a particular spot of the surface, the patch contaminated with ether starts spreading, i.e., displacement commences.

As mentioned in section 51, some investigators believe that foam-breakers should be used as emulsion droplets. Perhaps the powerful action of droplets is due simply to the fact that in a droplet of foam-breaker there is more of this substance than in a comparable volume of its dilute solution. When the ether-contaminated patch on the beer surface expands, the ether concentration in the surface layer decreases, and consequently γ_2 increases. To keep $\gamma_2 + \gamma_{12}$ smaller than γ_1, more ether must be supplied. Such a supply of foam-breaker is facilitated when a store of it is present as droplets distributed in the surface.

Formula (10) has often been cited as explanation for the destruction of foam by antifrothers. However, its quantitative experimental proof could not be found in the literature. Often γ_2 is identified with the equilibrium surface tension of A + C, and term γ_{12} is neglected. Thus the rule emerges that more surface-active substances displace those less surface active. Naturally, when B and C freely mix in the surface layer, there is no direct displacement and the rule cannot be expected to hold.

Qualitative determinations of the effect of additions on the foaming capacity of sodium bis-(2-ethylhexyl) sulfosuccinate in triethanolamine, diethylene glycol, and water, of an aromatic sodium sulfonate in water, and of oleic acid in triethanolamine, have been reported[107]. The results as well as the (again qualitative) data of Robinson and Woods[108] and of Pattle[109] are in general agreement with expression (10).

When the amount of C is so large that two layers form in the A + B + C system, the foaming capacity seems to depend above all on the relative amounts of the two layers and the difference between their surface tensions[110]. Thus in the two-phase mixtures of water, acetic acid, and benzene (their vapor forming the third phase), considerable foaminess is observed only when the total amount of water (i.e., in both layers together) greatly exceeds the combined amounts of the other constituents. In this case, the volume of the aqueous layer is much greater than that of the benzene layer and, on shaking, the benzene phase is emulsified in the aqueous phase so that air is in contact with a liquid (dilute solution of acetic acid and benzene in water) possessing considerable capacity for foaming. This would

appear to be a sufficient explanation for the foaming of mixtures rich in water, but Sasaki in addition postulates that the air bubbles formed in the aqueous phase are lined with a thin film of the benzene phase which goes into the air-liquid boundary because its surface tension is less than that of the aqueous phase. Sasaki believes also that a similar film, rich in benzene, exists along the interface between the liquid and the atmosphere and that every bubble stopped under this interface is separated from the outside air by a triple film of benzene phase—aqueous phase—benzene phase.

Section 48. *Foam formation in ternary mixtures.* A second solute may affect the ease of foam formation and thus simulate an effect on the foaming capacity.

If, as proposed in section 47, the dispersion of the upper (benzene) layer in the lower one really is essential for two-phase systems to foam when shaken, these systems would be excellent instances of the dependence of foaminess on the method of testing. In the bubbling procedure, used instead of shaking, air bubbles would rise through the two layers without causing any considerable emulsification and would burst immediately on reaching the boundary between liquid and the atmosphere, as the benzene-rich liquid does not froth.

However, a second solute can simulate an alteration of foaminess also in the bubbling method. When the dimension of the bubbles is not controlled by the experimenter, the second solute may affect bubble size at a capillary orifice or on an extended surface (see section 12). This effect is observed in the suppression of foam in boiling liquids and may play a part in the destruction of foam, produced by bubbling air through lubricants, by polysiloxanes[94].

Foam volume remaining after shaking or whipping may be reduced by a second solute if this increases the viscosity of the solution and thus renders incorporation of air more difficult (see section 26).

Section 49. *Glass, metal, and slag foams.* The stability of these foams has a mechanism different from the mechanism stabilizing the majority of the foams mentioned in the previous sections (see section 95).

Solid foams of glass, polystyrene, and other thermoplastic materials are used for heat and sound insulation (see Chapter 14). The foam

which may cover the surface of molten glass in glass furnaces apparently has not been investigated scientifically.

The similarity between the grain structure of alloys and the cell structure of foams was emphasized by Desch[111]. Foaming of bearing metal (an alloy of mainly lead and antimony) containing copper and iron was observed and attributed to formation of (surface active?) high melting alloys[112].

According to Evans[113], in open-hearth furnaces foaming was usually connected with high iron or high silica contents of the slag or with large carbon concentration in the metal. However, the luminosity of the flame heating the metal and slag from above is said to be more important than the chemical composition. When the flame is not luminous, the lower strata of the slag layer are supposed to be cool, and stable foam results. Luminous flame is supposed to heat the whole thickness of the slag layer, thus giving rise to more evanescent foam. According to Maibaum[114], blast furnace slags foam at 1390 to 1420° when they contain more than 35 per cent of silica or more than 44 per cent of (silica + alumina) and less than 50 per cent calcium oxide.

Section 50. *The composition of the gas phase.* In principle, the composition of the gas phase of foams is as important as that of the liquid phase. However, almost no systematic study of this problem has been carried out (see section 45). It appears that foam persistence is smaller when the gas is more soluble and/or has a greater diffusion coefficient in the liquid film, or when the gas chemically changes the frother making it less "active." When the chemical change results in a more "active" frother, the gas yields a more persistent foam.

The latter mechanism probably was responsible for the higher values of h/u (see section 22) observed when bubbling carbon dioxide rather than air through 0.01 per cent albumin solution[83]. Carbon dioxide caused visible coagulation of the protein and raised the ratio h/u to 190 to 240 sec as compared with 32 to 36 sec in air.

The stability of (apparently) protein foams is said to be less when carbon dioxide or sulfur dioxide is the gas than when the gas phase is air[60]; this would be an instance of the effect of solubility and diffusion. It is more difficult to account for the statement that the foaminess of gelatin solutions increases from air to nitrogen to carbon dioxide to oxygen[82].

Clark and Blackman[115] investigated the effect of the gas nature on the *specific surface* of an "aluminum protein hydrolysate" foam. Specific surface is defined as $\pi\Sigma(n_1d_1 + n_2d_2 + \ldots)$; Σ signifies the sum, and n_1, n_2, ... are the numbers of bubbles having diameters d_1, d_2, ... in unit layer of foam. When air was used, the specific surface decreased from the original value of about 300 cm (the unit volume was 1 cm^3) to 100 cm in about 2,500 sec. This process required less than 2,000 sec in oxygen and less than 500 sec in carbon dioxide. The specific surface was 50 cm in oxygen after about 5,500 sec and in carbon dioxide after about 1,000 sec. The effects of solubility and diffusion rate are probable also in this instance (see also section 66).

Section 51. *Foaming of emulsions.* With a few exceptions (sections 47 and 48), the foregoing stability data refer to two-phase systems. The stability of three-phase foams in which the third phase is solid is discussed in Chapter 11. The few data on the persistence of foams in emulsions (two liquid and a gas phase) are collected here.

It has been stated that a foam inhibitor should be an emulsion[116, 108] (see section 47). Some polysiloxanes depress the foam height (in the pneumatic method) of light mineral oil only when used in concentrations exceeding that of saturation[94]. This would imply that emulsions do not foam. The increase of foaminess by removal of suspended droplets (see section 42) agrees with this conclusions. Still it cannot be said generally that frothing is incompatible with emulsions. Thus oleic acid emulsions are stated to be froth inhibitors (in the production of yeast on molasses broth) only when their globules are between 1 and 10 μ (i.e., 10^{-4} and 10^{-3} cm) across[117]. Emulsions of crude oil and water froth when heated[118]. Cream is an emulsion which can be converted into a very stable foam (whipped cream).

Apparently the foaming capacity greatly depends on the type of emulsion, either water-in-oil (W/O) or oil-in-water (O/W). In water-benzene emulsions stabilized by albumin, foaming occurred if the emulsion was O/W but was absent in W/O systems[78]. Sasaki[13, 119] could prepare either O/W or W/O emulsions in mixtures of, for example, 2.33 cm^3 acetic acid, 3.79 cm^3 ether, and 3.88 cm^3 water by changing the details of shaking (see section 25). The W/O emulsions did, and the O/W emulsions did not, foam. In the system of acetic acid, benzene, and water, on the contrary, O/W emulsions only gave rise to foam.

Teitelbaum[96] pointed out that emulsification in the surface layer, whose concentration is different from the bulk concentration C, may take place at a C below that of saturation concentration in the bulk. If such a surface emulsion is present, the solution is expected to foam only when the emulsion is of the O/W type, as otherwise the "oily" outside phase will reach the surface and break the foam. Teitelbaum considers this hypothesis to be in accord with the temperature effects on the persistence of methanol-mesitylene foams (section 52).

Foaminess and Temperature

Section 52. Foam persistence usually is less at higher temperatures. A more definite statement is not possible, as, in theory, temperature can affect foaminess in many different ways, and the temperature effects observed often are sums of independent effects whose magnitude has not been ascertained by experiment. This is particularly true of the highly complex systems which, unfortunately, have been more often studied at different temperatures than simple systems. In a simple system, namely 0.05M aqueous isoamyl alcohol, the time of collapse of foam (after shaking) was at 50° by 32 per cent shorter than at 18°[14].

The foam volumes (after shaking) of 0.25 per cent solutions of potassium oleate, potassium laurate, and potassium myristate were identical at 30° and 70°[33]. The temperature dependence of the foam volume of solutions of sodium alkyl sulfates is treated in section 40. The foam height (after pouring) of dilute solutions of condensation products of higher alcohols and ethylene oxide was at 50° by about 25 per cent greater than at 20°[52a].

When 25 cm^3 of 1 per cent gelatin (containing 10 per cent peptones) solution was shaken at 20, 40, 50, 60, 70, 80, 90, and 100°, the foam height was 30.0, 25.5, 20.0, 15.0, 13.0, 11.0, 5.5, and 3.5 arbitrary units, respectively[77]. There are data on the temperature coefficient of foaminess of other protein solutions[119a], milk[120, 121, 121a], honey[122], eggs[123], beer[124], sulfite liquor[125], and so on.

The value of L_g (see section 28) of hydrocarbon oils was smaller the higher the temperature; it was, for example, 32 min. at 26° and 1.15 min. at 100°[92]. Also in Trautman's experiments[94] foaminess of hydrocarbon oils decreased when temperature was raised from 24 to 150°, but oils containing detergents frothed at high more than at low temperature. The lifetime of a single bubble (diameter 0.3 cm)

of an equimolecular mixture of nitrobenzene and hexane was 12 sec at 0° and 7 sec at 10°[95a].

Fig. 29 demonstrates how complex the influence of temperature on

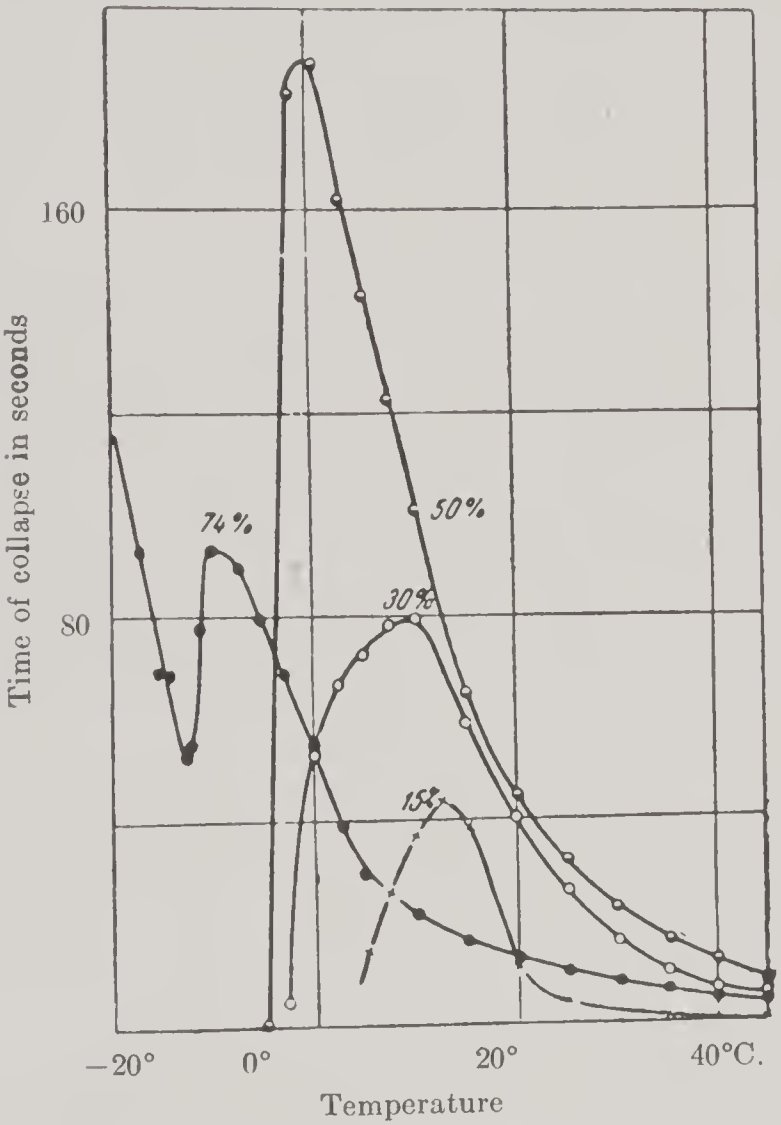


FIGURE 29. Effect of temperature on the time of collapse of mesitylene-methanol foams. Figures at the curves are molecular percents of methanol. From *Kolloid. Zhur.*, **12**, 381 (1950).

foaminess can be[96]. Temperature is plotted along the abscissa; the ordinate is the time of collapse, t, after shaking; and the percentages at the curves mean the molecular per cent of methanol in its mixtures with mesitylene. The existence of maxima of t is a striking feature of the curves. It is possible that, in other instances, such maxima may be brought about by a tug-of-war between two viscosity effects: decrease of viscosity at higher temperatures would augment the

volume of foam produced by a standard shaking (see section 26) and at the same time reduce the lifetime of every film (see section 102). If the first effect exceeds the second at low, and is exceeded by it at high, temperatures, a maximum of t may result. However, in the instance of Fig. 29 the low values of t at temperatures below the maximum undoubtedly are related to solubility. The 30 per cent and the 50 per cent solutions form two layers a few degrees below 0°, i.e., at the temperatures at which their t becomes very small. The 74 per cent system is heterogeneous below −12°, i.e., at the minimum of t. The two-phase systems containing 30 and 50 per cent methanol did not, and the two-phase system containing 74 per cent methanol did foam, perhaps because the former gave rise to methanol-in-mesitylene and the latter to mesitylene-in-methanol emulsions (see section 51).

References

1. Plateau, J., *Mém. acad. roy. sci. Belgique*, **37**, 52 (1869). 8th ser.
2. Foulk, C. W., and Barkley, J. E., *Ind. Eng. Chem.*, **35**, 1013 (1943).
3. Talmud, D., and Sukhovolskaya (Suchowolskaja), S., *J. Phys. Chem. (U.S.S.R.)*, **2**, 31 (1931); *Z. physik. Chem.*, **154A**, 277 (1931).
4. Leaf, W., *et al.*, *Am. Ry. Eng. Assoc.*, **45**, *Bull.*, **441**, 58 (1943).
5. Hancock, J. S., *J. Soc. Chem. Ind.*, **49**, 369T (1930).
6. Leaf, W., *et al.*, *Am. Ry. Eng. Assoc.*, **46**, *Bull.*, **448**, 59 (1944).
7. Foulk, C. W., and Ryznar, J. W., *Ind. Eng. Chem.*, **31**, 722 (1939).
8. Durov, S. A., *J. Applied Chem. (U.S.S.R.)*, **13**, 693 (1940).
8a. Fesenko, N. G., *Doklady acad. sci. U.S.S.R.*, **72**, 547 (1950).
8b. Miyake, Y., *Science (Japan)*, **13**, 358 (1943); *Chem. Abs.*, **45**, 9935 (1951).
9. Bikerman, J. J., "Surface Chemistry for Industrial Research," New York, Academic Press, 1948.
10. Schütz, F., *Trans. Faraday Soc.*, **38**, 94 (1942).
11. Nakagaki, M., *Bull. Chem. Soc. Japan*, **22**, 21 (1949).
12. Gibb, W., and Htin, K., *J. Roy. Tech. Coll. (Glasgow)*, **5**, 128 (1950).
13. Sasaki, T., *Bull. Chem. Soc. Japan*, **14**, 250 (1939).
14. Bartsch, O., *Kolloidchem. Beihefte*, **20**, 1 (1924).
15. Sasaki, T., *Bull. Chem. Soc. Japan*, **13**, 517 (1938).
16. Bikerman, J. J., *Trans. Faraday Soc.*, **34**, 634 (1938).
17. Rebinder (Rehbinder), P., and Venstrem (Wenström), E., *Kolloid-Z.*, **53**, 145 (1930).
18. Lubman, N. M., *J. Phys. Chem. (U.S.S.R.)*, **3**, 204 (1932); *Tsvetnye Metal.*, **6**, 854 (1931).
19. Aleinikov (Alejnikoff), N. A., *Tsvetnye Metal.*, **6**, 1546 (1931); *Kolloidchem. Beihefte*, **36**, 82 (1932).
20. Rebinder (Rehbinder), P., and Trapeznikov, A., *Acta physicochim. U.S.S.R.*, **9**, 257 (1938).
21. Nakagaki, M., *Bull. Chem. Soc. Japan*, **23**, 127 (1950).

22. Ross, S., *J. Phys. Chem.*, **50,** 391 (1946).
23. Nakagaki, M., *Bull. Chem. Soc. Japan*, **21,** 30 (1948).
24. Haefele, C. R., *Paper Trade J.*, **126,** No. 15, 66 (1948).
25. Sasaki, T., *Bull. Chem. Soc. Japan*, **13,** 669 (1938).
26. Talmud, D. L., *J. Phys. Chem. (U.S.S.R.)*, **5,** 1062 (1934).
27. Taggart, A. F., and Gaudin, A. M., *Trans. Am. Inst. Mining Met. Engrs.* **68,** 479 (1923).
28. Merrill, R. C., and Moffett, F. T., *Oil & Soap*, **21,** 170 (1941).
29. Bikerman, J. J., *J. Phys. Chem.*, **56,** 164 (1952).
30. Burcik, E. J., *J. Colloid Sci.*, **5,** 421 (1950).
31. Miles, G. D., and Ross, J., *J. Phys. Chem.*, **48,** 280 (1944).
32. Götte, E., *Melliand Textilber.*, **29,** 65, 105 (1948).
33. Reutenauer, G., and Sicard, P., *Bull. mens. ITERG*, **4,** 99 (1950); *Chem. Abs.*, **44,** 5621 (1950).
34. Pankhurst, K. G. A., *Trans. Faraday Soc.*, **37,** 496 (1941).
35. Johlin, J. M., *J. Biol. Chem.*, **84,** 543 (1929).
35a. Shkodin, A. M., and Tikhomirova, G. P., *Kolloid. Zhur.*, **14,** 279 (1952).
35b. Mysona, M., and Rylko, K., *Przemysl Chem.*, **6** (**29**), 254 (1950); *Chem. Abs.*, **45,** 10623 (1951).
36. Morrisroe, J. J., and Newhall, R. G., *Ind. Eng. Chem.*, **41,** 423 (1949).
37. Dedrick, C. H., and Wills, J. H., *Ind. Eng. Chem.*, **41,** 575 (1949).
38. Lederer, E., *Angew. Chem.*, **47,** 119 (1934).
39. Fiero, G. W., *J. Am. Pharm. Assoc.*, **27,** 658 (1938).
40. Plateau, J., *Mém. acad. roy. sci. Belgique*, **36,** (1867). 7th ser.
41. Dewar, J., *Proc. Roy. Inst. Gt. Brit.*, **24,** 197 (1925).
42. Cook, G. A., *J. Chem. Education*, **15,** 161 (1938).
43. Bragg, L., and Nye, J. F., *Proc. Roy. Soc. (London)*, **190A,** 474 (1947).
44. Kuehner, A. L., *J. Chem. Education*, **25,** 211 (1948).
45. Götte, E., *Kolloid-Z.*, **64,** 327 (1933).
46. Dreger, E. E., *et al.*, *Ind. Eng. Chem.*, **36,** 610 (1944).
47. Winsor, P. A., *Nature*, **157,** 660 (1946).
48. Dean, R. S., and Hersberger, A. B., *Trans. Am. Inst. Mining Met. Engrs.*, **134,** 81 (1939).
49. Sabetay, S., *Bull. soc. chim. France* [5]**3,** 1918 (1936).
50. Savitskaya, E. M., and Rebinder, P. A., *Kolloid. Zhur.*, **13,** 200 (1951).
50a. Paquot, C., *J. recherches centre natl. recherche sci. Labs. Bellevue (Paris)*, **1950,** 169; *Chem. Abs.*, **45,** 10617 (1951).
51. Reutenauer, G., Frelat, M., and Sicard, P., *Bull. mens. ITERG*, **3,** 448 (1949); *Chem. Abs.*, **44,** 2772 (1950).
52. Vaughn, T. H., *et al.*, *J. Am. Oil Chemists' Soc.*, **28,** 294 (1951).
52a. Baldacci, R., *Ann. chim. (Rome)*, **40,** 358, 372 (1950).
52b. Raison, M., and Matalon, R., *Mém. services chim. état (Paris)*, **34,** 353 (1948).
53. Hardy, W. B., *Proc. Roy. Soc. (London)*, **86A,** 610 (1912); *J. Chem. Soc.*, **127,** 1207 (1925).
54. Trapeznikov, A. A., *Acta physicochim. U.R.S.S.*, **13,** 265 (1940).
55. Isemura, T., *J. Chem. Soc. Japan*, **64,** 1016 (1943); *Chem. Abs.*, **41,** 3343 (1947).

56. Taggart, A. F., Taylor, T. C., and Ince, C. R., *Trans. Am. Inst. Mining Met. Engrs.*, **87,** 285 (1930).
57. Horiuchi, R., Todo, N., and Kishi, Y., *J. Soc. Chem. Ind. Japan*, **45,** Suppl. binding, 110 (1942); *Chem. Abs.*, **44,** 9881 (1950).
58. Rebinder, P., *Bull. acad. sci. U.R.S.S., Classe sci. math. nat., Sér. chim.*, **1936,** 639.
58a. Shiou-Chuan Sun, *Mining Eng.*, **4,** 65 (1952).
58b. Aleinikov, N. A., *Zhur. Priklad. Khim.*, **22,** 812 (1949).
59. Ruyssen, R. G., and Verstraete, E. O. K., *Mededeel. Koninkl. Vlaam. Acad. Wetenschap. Belg., Klasse Wetensehap.*, **4** (6) (1942); *Chem. Abs.*, **38,** 3889 (1944).
60. Dumanskii, A. V., Granskaya, T. A., and Novikov, N. V., *Schriften zentral. biochem. Forseh. Inst. Nahr. u. Genussmittelind. (U.S.S.R.)*, **3,** 361 (1933); *Chem. Abs.*, **28,** 2970 (1934).
61. Sasaki, T., *Bull. Chem. Soc. Japan*, **15,** 449 (1940).
62. Schütz, F., *Trans. Faraday Soc.*, **38,** 85 (1942).
63. Plateau, J., *Mém. acad. roy. sei. Belgique*, **37,** 98 (1869). 8th ser.
64. Mitsui, S., and Sasaki, T., *Bull. Chem. Soc. Japan*, **18,** 259 (1943); *Chem. Abs.*, **41,** 4352 (1947).
65. Kind, W., and Zschacke, F. H., *Z. deut. Öl- u. Fett-Ind.*, **43,** 520 (1923).
66. Tyutyunnikov, B., Kasyanova, N., and Gvirtsman, N., *Maslobožno-Zhirovoe Delo*, **1930,** No. 7–8, 48; *Allgem. Öl- u. Fett-Ztg.*, **27,** 273 (1930); *Chem. Abs.*, **25,** 2317 (1931).
67. Shkodin, A. M., and Tikhomirova, G. P., *Kolloid. Zhur.*, **13,** 134 (1951).
68. Holwerda, K., *Biochem. Z.*, **295,** 11 (1937).
69. Bader, R., and Schütz, F., *Trans. Faraday Soc.*, **42,** 571 (1946).
70. Bogue, R. H., *J. Am. Chem. Soc.*, **44,** 1343 (1922).
70a. Peters, D., *Kolloid-Z.*, **125,** 157 (1952).
71. Mischke, W., *Kolloid-Z.*, **90,** 77 (1940).
72. Loebel, Z. C., *J. Phys. Chem.*, **32,** 763 (1928).
73. Thuman, W. C., Brown, A. G., and McBain, J. W., *J. Am. Chem. Soc.*, **71,** 3129 (1949).
74. Perri, J. M., and Hazel, F., *J. Phys. & Colloid Chem.*, **51,** 661 (1947).
75. Sthamer, R., British Patent 476,552; French Patent 823,922; *Chem. Abs.*, **32,** 4257 (1938).
76. Clark, N. O., "A Study of Mechanically Produced Foam for Combating Petrol Fires," p. 55, London, Dept. Sci. Ind. Res., 1947.
77. Trotman, S. R., and Hackford, J. E., *J. Soc. Chem. Ind.*, **25,** 104 (1906).
78. Dumanskii, A. V., Granskaya, T. A., and Vishnevskaya, G. R., *Izvest. Gosudarst. Nauch.-Issledovatel. Inst. Kolloid. Khim.*, No. 1, 96 (1934); *Chem. Abs.*, **34,** 5201 (1940).
79. Hadorn, H., *Mitt. Gebiete Lebensm. u. Hyg.*, **38,** 46 (1947); *Chem. Abs.*, **41,** 5053 (1947).
80. Sauer, E., and Aldinger, W., *Kolloid-Z.*, **88,** 329 (1939).
81. Tarassuk, N. P., and Richardson, G. A., *Proc. 23rd Ann. Meeting Western Div., Am. Dairy Sci. Assoc.*, **1937,** 70; *Chem. Abs.*, **32,** 1795 (1938).
82. Viktorin, O., *Chem. Listy*, **34,** 265, 283 (1940); *Chem. Abs.*, **43,** 8794 (1949).
83. Clark, G. L., and Ross, S., *Ind. Eng. Chem.*, **32,** 1594 (1940).

84. Ermolenko, N. F., and Abramchuk, N. A., *J. Phys. Chem. (U.S.S.R.)*, **8,** 587 (1938).
85. Ostwald, Wo., and Steiner, A., *Kolloid-Z.*, **36,** 342 (1925).
86. Pattle, R. E., *J. Soc. Chem. Ind.*, **69,** 369 (1950).
87. Morrison, R. I., and Campbell, B., *J. Soc. Chem. Ind.*, **68,** 333 (1949).
88. Breitner, H. J., *Kolloid-Z.*, **100,** 335 (1942); **101,** 31 (1942).
89. Nakagaki, M., *Bull. Chem. Soc. Japan*, **22,** 200 (1949).
90. Nakagaki, M., *Bull. Chem. Soc. Japan*, **23,** 47 (1950).
91. Bresler, S. E., and Talmud, D. L., *J. Phys. Chem. (U.S.S.R.)*, **4,** 796 (1933).
92. Brady, A. P., and Ross, S., *J. Am. Chem. Soc.*, **66,** 1348 (1944).
93. Robinson, J. V., and Woods, W. W., *J. Phys. & Colloid Chem.*, **52,** 763 (1948).
94. Trautman, C. E., *Lubricating Eng.*, **2** (4), 143 (1946).
95. McBain, J. W., *et al.*, Natl. Advisory Comm. Aeronautics, Tech. Notes 1840, 1841, 1842, 1845 (1949).
95a. Teitelbaum, B. Ya., and Sidorova, E. E., *Kolloid. Zhur.*, **14,** 372 (1952).
96. Teitelbaum, B. Ya., *Kolloid. Zhur.*, **12,** 375 (1950).
97. King, E. G., *J. Phys. Chem.*, **48,** 141 (1944).
98. Hartner-Seberich, R., *Ges. Abhandl. Kenntnis Kohle*, **11,** 628 (1934).
99. Wada, T., *J. Chem. Soc. Japan*, **65,** 369, 440 (1944); *Chem. Abs.*, **41,** 3309 3983 (1947).
100. Naudet, M., Micaelli, O., and Denuelle, P., *Bull. mens. ITERG*, **1948,** No. 6, 32.
101. Dieterle, R., *Seifensieder-Ztg.*, **66,** 54 (1939); *Chem. Abs.*, **33,** 9693 (1939).
102. Ritter, W., *Mitt. Lebensm. Hyg.*, **29,** 253 (1938); *Chem. Abs.*, **33,** 2598 (1939).
103. Robinson, H. E., Black, H. C., and Mitchell, H. S., *Oil & Soap*, **17,** 208 (1940).
103a. Teitelbaum, B. Ya., and Ganelina, S. G., *Kolloid. Zhur.*, **14,** 267 (1952).
103b. Teitelbaum, B. Ya., *Kolloid. Zhur.*, **14,** 292 (1952).
103c. Gunderson, L. O., and Bodach, C. M., *R'y Engr. and Maintenance*, **47,** 447 (1951); *Chem. Abs.*, **45,** 8682 (1951).
104. Pokhil, P. F., *J. Phys. Chem. (U.S.S.R.)*, **14,** 554 (1940).
105. Quincke, G., *Ann. Physik*, **35,** 580 (1888).
106. Quincke, G., *Pogg. Ann.*, **139,** 1 (1870).
107. Ross, S., and McBain, J. W., *Ind. Eng. Chem.*, **36,** 570 (1944); Ross, S., *J. Phys. & Colloid Chem.*, **54,** 429 (1950).
108. Robinson, J. V., and Woods, W. W., *J. Soc. Chem. Ind.*, **67,** 361 (1948).
109. Pattle, R. E., *J. Soc. Chem. Ind.*, **69,** 363 (1950).
110. Sasaki, T., *Bull. Chem. Soc. Japan*, **14,** 3 (1939).
111. Desch, C. H., *Rec. trav. chim.*, **42,** 822 (1923).
112. Wolfenden, E. A., *Metal Progress*, **50,** 479 (1946).
113. Evans, R. W., *Blast Furnace Steel Plant*, **32,** 932 (1944).
114. Maibaum, D., see Keil, F., *Stahl u. Eisen*, **62,** 1091 (1942).
115. Clark, N. O., and Blackman, M., *Trans. Faraday Soc.*, **44,** 1 (1948).
116. Fiske, C. H., *J. Biol. Chem.*, **35,** 411 (1918).
117. Metyushev, B. D., and Kharin, S. E., *Gosudarst. Nauch-Issledovatel. Inst.*

Kolloid. Khim., Tekhnol. Protsessy i Kontrol Pishchevoi Ind., **1938,** 149; *Chem. Abs.*, **32,** 9388 (1938).

118. Egloff, G., and Berkman, S., *J. Phys. Chem.*, **39,** 265 (1935).
119. Sasaki, T., *Bull. Chem. Soc. Japan*, **14,** 63, 107 (1939).
119a. Oehman, V., *Tek. Tid.*, **82,** 317 (1952); *Chem. Abs.*, **46,** 6461 (1952).
120. Mohr, W., and Brockmann, C., *Milchw. Forsch.*, **11,** 48 (1930); *Chem. Abs.*, **25,** 1916 (1931).
121. Sirks, H. A., *Verslag. Landbouwk. Onderzoek., Rijkslandbouwproefsta.*, No. **41C,** 461 (1935); *Chem. Abs.*, **30,** 2649 (1936).
121a. Richardson, G. A., and El-Rafey, M. S., *J. Dairy Sci.*, **31,** 223 (1948); *Chem. Abs.*, **45,** 274 (1951).
122. Milum, V. G., *Am. Bee J.*, **79,** 186 (1939); *Chem. Abs.*, **33,** 4337 (1939).
123. Hawthorne, J. R., and Bennion, E. B., *J. Soc. Chem. Ind.*, **61,** 153 (1942).
124. Helm, E., and Richardt, O. C., *J. Inst. Brewing*, **42,** 191 (1936).
125. Smirnov, V. A., and Bondarenko, A. N., *J. Applied Chem. (U.S.S.R.)*, **20,** 97 (1947).

4. FOAM DRAINAGE

Section 53. The rate of drainage of a foam has often been used as measure of "foaming capacity," "foaming power," and so on. In this book it is treated in a chapter apart, separately from foam stability, to emphasize the fact that drainage and persistence of foams are entirely different phenomena.

Foam exists as long as the films constituting it exist. This statement is in agreement not only with the definition of section 1, but also with the use of the word *foam* in daily life. When foam on beer, on a seashore, on boiling milk, etc., is mentioned, no minimum thickness of the lamellae is implied. Drainage is, first of all, thinning of the foam lamellae without any rupture. If the foam is very stable, this "pure drainage" can be measured directly. It is true, however, that in the usual methods for the determination of drainage, the liquid originating from unbroken lamellae cannot be differentiated from that yielded by ruptured films. Thus usually the liquid leaving the foam has two distinct origins and no definite physical significance.

Section 54. All *procedures for measuring the rate of drainage* are similar. Foam is produced by bubbling or agitation and then left alone, and the liquid which collects under the foam column is measured by weight or volume at one or at different times.

Fig. 30 illustrates an apparatus[1] which was popular in Germany. It is a flask consisting of a bulb (1,900 cm^3 capacity), a connecting tube (50 cm^3), and another bulb (50 cm^3). 100 cm^3 of liquid are shaken in it for 30 sec, then the flask is placed with the smaller bulb down, and the liquid volume is read after 3 min. Call this volume x cm^3; then $100 - x$ is the "foam number." In another variant[2] a smaller flask (total volume 100 cm^3) was used and the liquid volume was read after 1 min.

In the "Carlsberg method" of determining the "foaming capacity" of beer[3] "the foam is formed in a natural way, viz., by the free fall of the beer." The foam is allowed to drain, and the liquid is collected after 2 min. (volume a) and after 10 minutes (volume b); then the remaining foam is destroyed and the resulting liquid measured (vol-

ume c). The ratio $100(b + c)/(a + b + c)$ is designated the total foam or the total head, and the ratio $100\ c/(a + b + c)$ is the residual foam or the residual head.

In a modification of this procedure[3a] beer is saturated with carbon dioxide under pressure, the pressure is released, and the foam formed

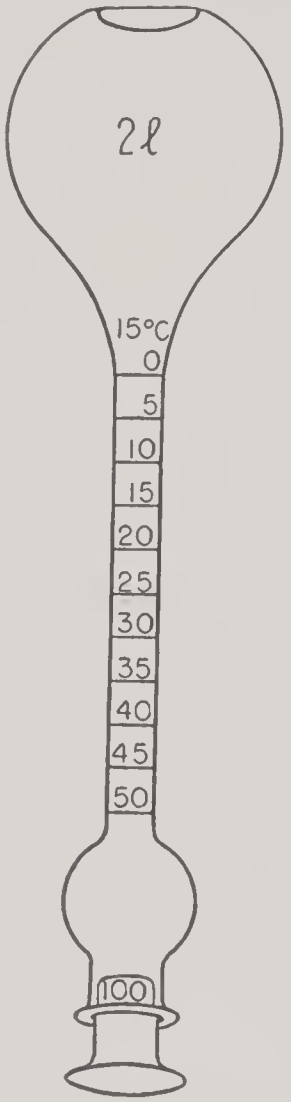


FIGURE 30. A flask for determining the rate of drainage ("foam number"). From *Seifensieder-Ztg.*, **41**, 347 (1914).

is forced into a vertical cylinder of 100 cm^3 until this is full. Then the volume of the liquid beer is read every minute for 8 minutes, the rest of the foam is destroyed by isopropyl alcohol, and the final (total) liquid volume is measured. If this final volume is A, and the volumes after 1, 4, 5, and 8 minutes are a, b, c, and d, respectively, then $50(b + c - a - d)/A$ is the "foam index" of beer.

Egg white foam was produced by whipping. The mass M_1 of foam was allowed to drain for an hour. If the mass of the liquid obtained was M_2, the ratio $100\ M_1/M_2$ was "per cent leakage"[4].

A process intermediate between agitation and bubbling was used for soap solutions[5]. Air was introduced into the solution (volume V_1) through a horizontal tube rotating about a vertical axis and, presumably, was broken to smaller bubbles by the agitation. The stirring was continued for 2 min., which time presumably was sufficient to transfer the whole of the liquid into foam. Then the system was left alone for 1 min., and the volume collected (V_2) was measured. The ratio $100\ (V_1 - V_2)/V_1$ is "the foam power."

The pneumatic method of foam making (see section 21) was applied, for example, to vegetable and animal oils[6]. 100 cm^3 of air were bubbled through 25 cm^3 of oil. This usually resulted in complete transfer of oil into the foam. Then the air current was stopped, and the time determined for 12.5 cm^3 of oil to collect under the foam. This time was the "half-life" of the foam.

All the above methods for the determination of the rate of drainage are suitable for crude comparisons only. The arbitrariness of basing the final result on the volume drained out after 3, 1, or 10 min., an hour, etc., is obvious. However, even more serious is the absence of information on the changes produced in the rate of drainage by varying the shape and dimension of the apparatus employed, the details of agitation or bubbling, the amount of liquid used, and so on. It is often assumed that if the same apparatus, same rate of stirring, etc., are employed for different liquids, the figures obtained are strictly comparable. This assumption is not warranted (see, e.g., section 26). In the pneumatic method the influence of the rate (u) of gas flow on the foam height (h) is circumvented by using the ratio h/u as a measure of foaminess. The rate of drainage of pneumatic foam also depends on u; soap foams lose solution quicker the greater u is[7]. No correction for this effect has been suggested.

Section 55. The methods reported in section 54 can be improved by measuring the volume V of liquid separated from foam after several time intervals and representing V as function of time t either as a curve or by an equation. Curve b of Fig. 15, section 28, and Fig. 31 are examples of such functions; see also ref. 7.

The values represented in Fig. 31 have been obtained in a special apparatus[8] (see Fig. 32). A glass bulb carries a graduated tube at the bottom, a connection to vacuum line in a side wall, and a sintered glass funnel at the top. The liquid slowly drops onto the funnel and

is transformed into foam by the air sucked into the bulb through the porous glass plate. When 10 cm^3 of the liquid are thus transferred into foam, the vacuum connection is severed and the liquid flows into the graduated tube where its volume is read from time to time. In Fig. 31 the abscissa is time, and the ordinate represents the volume of liquid in the tube, divided by the original volume V_0 (i.e., 10 cm^3).

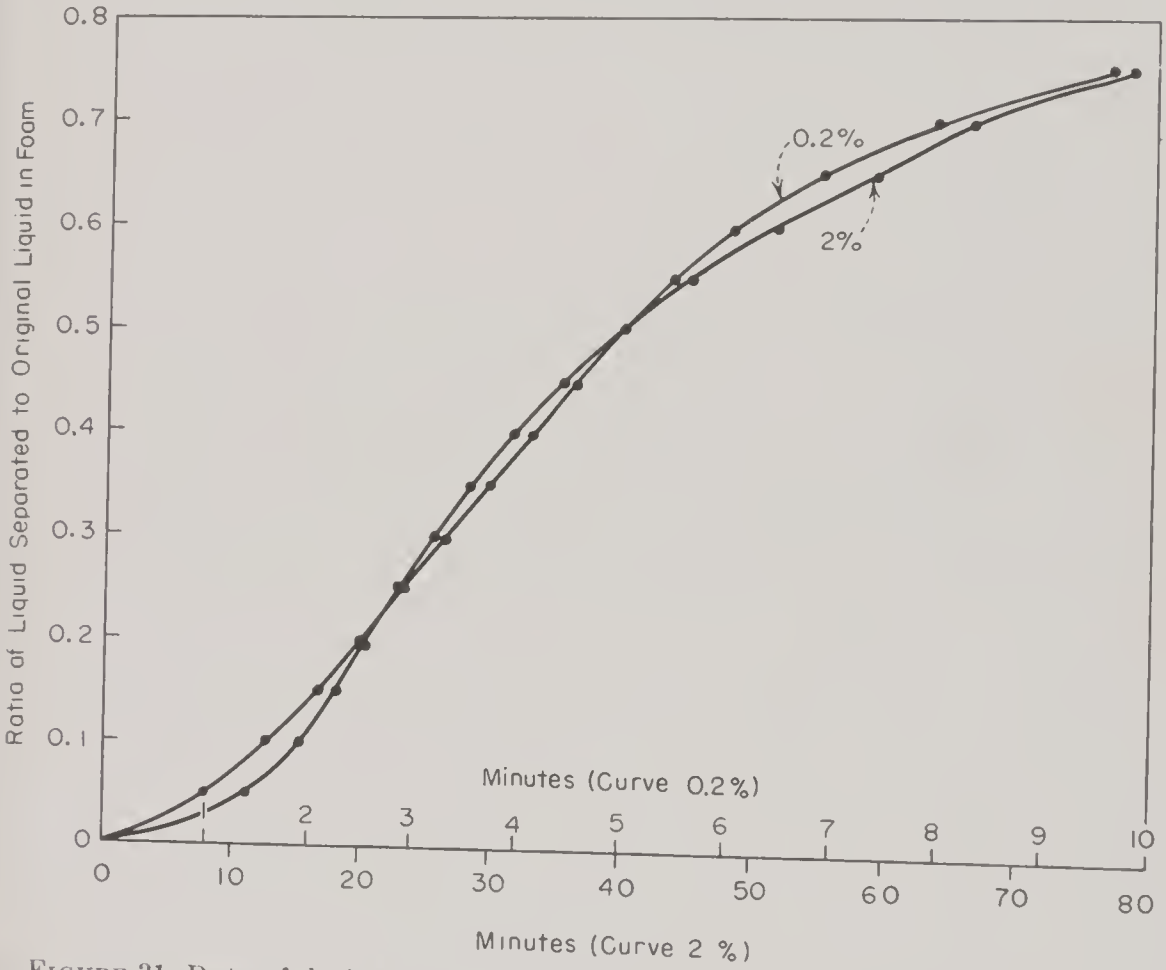


FIGURE 31. Rate of drainage of 0.2% and 2% saponin foams. Data of Arbuzov and Grebenshchikov[8].

Data for two saponin solutions, 0.2 and 2 per cent, are shown in the figure. The two curves are very similar but all changes in 2 per cent solution take eight times as many minutes as in 0.2 per cent solution. Unfortunately, the viscosity of these liquids has not been determined. It is seen that the rate of drainage (dV/dt) first increased, for a while remained constant (between the volume ratios V/V_0 0.15 and 0.5 for 0.2 per cent and 0.1 and 0.3 for 2 per cent solution), and then decreased. Arbuzov and Grebenshchikov point out the similarity of this behavior to syneresis of gels and describe drainage as *syneresis of*

foams. The variation of dV/dt with t is explained on the assumption that the liquid exuded originates from ruptured bubbles, i.e., is not due to drainage proper. It is further assumed that bubbles start bursting at the top of the foam column. The liquid liberated by this bursting takes time to reach the bottom tube; this would account for the increase of dV/dt in the first stage of collapse. The decrease of dV/dt in the third stage is attributed (*a*) to the obvious reason

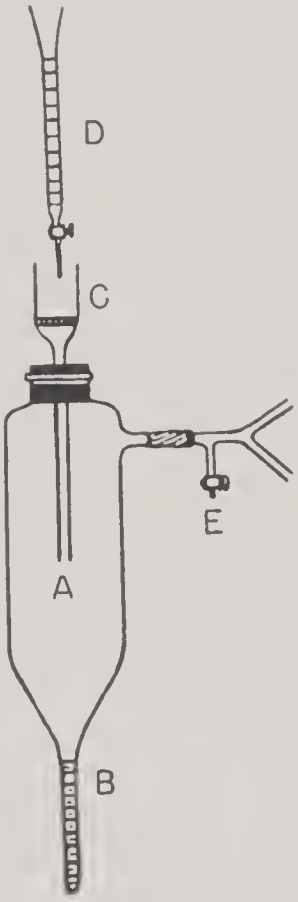


FIGURE 32. An apparatus for producing foam and measuring its rate of drainage. Liquid drops from D onto sintered glass filter C and is transformed into foam by air sucked through C into A by means of a vacuum pump attached to E. Then the foam is allowed to drain, and the volume drained is read in capillary B. From *J. Phys. Chem.* (*U.S.S.R.*), **10**, 32 (1937).

that there is less foam left to collapse, and (*b*) to the stabilization of foam caused by the gradual increase in the saponin concentration (the liquid exuded contains less saponin than the original liquid, see section 104). During the third stage of the process $V/V_0 = 1 - e^{-kt}$. The value of the constant k was 0.018 min.$^{-1}$ for 2 per cent solution and, as would be expected from Fig. 31, eight times as great (0.144 min.$^{-1}$) for 0.2 per cent solution.

A maximum of the rate of drainage at some middle value of V/V_0 is clearly visible also, for example, in the curves published by Barmore[9] for egg white foams produced by whipping with a kitchen mixer.

Table 7 assembles some mathematical expressions for the volume V exuded during time t and for the rate of drainage dV/dt. The original volume of liquid in the foam is V_0.

The first line of equations implies that the rate of drainage at any moment is proportional to the amount of liquid still present in the foam or, in other words, that drainage is a first-order reaction. The equation of Erbring (12) is that of a rectangular hyperbola. It cannot be correct as it requires volume V to be negative when t is very

TABLE 7. EQUATIONS FOR THE RATE OF DRAINAGE

Volume Exuded (V)		Rate of Drainage	References
$V = V_0(1 - e^{-kt})$	(11)	$\frac{dV}{dt} = kV_0e^{-kt} = k(V_0 - V)$	8, 10, 11
$V = V_0 - \frac{1}{kt}$	(12)	$\frac{dV}{dt} = \frac{1}{kt^2} = k(V_0 - V)^2$	12
$\frac{1}{(V_0 - V)^2} - \frac{1}{V_0^2} = 2kt$	(13)	$\frac{dV}{dt} = k(V_0 - V)^3$	13
$V = V_0(1 - e^{-k\sqrt{t}})$	(14)	$\frac{dV}{dt} = \frac{kV_0}{2\sqrt{t}} e^{-k\sqrt{t}} =$ $\frac{k^2(V_0 - V)}{2 \ln [V_0/(V_0 - V)]}$	14
$V_0 - V - a \log (V_0 - V) + b = kt$	(15)	$\frac{dV}{dt} = \frac{k(V_0 - V)}{a - V_0 + V}$	15

small. The differentiated form of the equation, when properly integrated, leads to expression

$$V = V_0^2kt/(1 + V_0kt)$$

as the function between V and t, which is entirely analogous to the equation for second-order reactions. Equation (13) would make drainage a third-order reaction. It is intended to be valid for drainage proper (no bursting!); then the proportionality between dV/dt and $(V_0 - V)^3$ has some theoretical justification (see section 56). Lederer's equation is given in the integrated form (14) in the original publication. The resulting expression for dV/dt makes clear that the rate of drainage would be infinitely great at the start of the experiment when $t = 0$ and $V = 0$; obviously the equation can be applicable, if at all, to later stages only. The arbitrary constant b in equation (15) can

readily be eliminated. The equation obtained

$$-V + a \log \frac{V_0}{V_0 - V} = kt$$

becomes identical with the first-order reaction if the second term on the left-hand side is much greater than the first. If the second term is much smaller than the first, the volume exuded would decrease in time, which is not possible. For theoretical deduction of equation (15), see section 56.

The "average lifetime of liquid in foam" was defined[16] as

$$L_1 = \frac{1}{V_0} \int_0^{V_0} t dV$$

(see section 28). It naturally is related to constant k of equations (11) to (15). For example, if equation (11) is valid, then $L_1 = \frac{1}{k}$. If half the liquid initially present in foam has drained within T_1 seconds, T_1 is the half-life time of the foam. It also is related to k. If, again, equation (11) is valid, $T_1 = \frac{0.693}{k}$.

According to Brenner *et al.*[3a], the curve of V versus t (for beer) consists of two parts. The first part is linear and corresponds to "pure drainage" (section 53), while the second is an exponential curve and due to coalescence and bursting of bubbles.

Section 56. The *mechanism of drainage* was described by Plateau[17]. If the foam film is not horizontal, the liquid drains because of (*a*) gravitation and (*b*) suction by Plateau's border (section 15). In a horizontal film only the second agent is operative. To have an idea of the relative importance of these two factors, let us consider an aqueous foam h cm high. The pressure due to gravitation is then 981 h dynes/cm^2. The suction due to Plateau's border is (approximately) γ/R_2, γ being the surface tension and R_2 the smaller radius of curvature of the surface of the border. The value of γ would rarely be less than 30 g/sec^2; hence the suction would be at least $30/R_2$ dynes/cm^2. Hence, factor (*b*) exceeds factor (*a*) in importance as long as R_2 is less than $0.03/h$ cm. For example, in a foam 1 cm tall, R_2 should be less than 0.03 cm. Doubtless even smaller radii of curvature are common in foams, but measurements of R_2 would be highly welcome.

A satisfactory calculation of the rate of drainage due to gravitation would be possible if we knew the geometry of the capillary system in which the movement takes place. As this knowledge is not available, assumptions must be made. Gibbs[18] treated the foam as a slit between two immovable parallel plates. The mean velocity of descent in such a slit is

$$u = \rho g \delta^2 / 12\eta \tag{16}$$

if ρ is the density of the liquid (minus that of the gas), g the acceleration due to gravity, δ the distance between the plates, and η the viscosity of the liquid. For water at 20° this velocity is 8,170 δ^2 cm/sec, δ being in cm. In a film 10^{-4} cm thick, water would flow at the rate of about 8×10^{-5} cm/sec.

A better approximation was made by Brady and Ross[13]. When liquid drains from a foam film, the film thins. Thus the parallel plates between which the descent takes place are not immobile; their mutual distance may be assumed to be proportional to the liquid content of the foam, i.e., to $V_0 - V$. If H is the height and L the width of the plates, then the volume of the slit and of the liquid filling it is $HL\,\delta$, i.e., $\delta = (V_0 - V)/HL$. The volume rate of flow between two parallel walls is

$$\frac{dV}{dt} = \frac{L\rho g \delta^3}{12\eta} \tag{17}$$

(see equation (16)). Introduction of δ from the preceding equation yields

$$\frac{dV}{dt} = \frac{\rho g (V_0 - V)^3}{12\eta H^3 L^2} \tag{18}$$

Hence, constant k in equation (13) is $\rho g/12\eta\ H^3L^2$. It is seen that this constant should be inversely proportional to the cube of the height of the foam column. No confirmation of this deduction could be found in the literature.

Foam has been pictured also as a bundle of cylindrical capillaries, and it was assumed that the liquid column in each capillary is capped with a meniscus which exerts capillary pressure modifying the effect of gravitation[15]. Unfortunately, no air has been seen between the surface films in a foam lamella so that the existence of the menisci postulated is doubtful. Some additional assumptions are needed to arrive from the hypothesis stated to equation (15). The pull exerted

on the liquid by the capillary pressure acting along Plateau's borders is not considered in this theory either.

The comparison of foam network with a bundle of cylindrical capillaries may be less inexact than appears at first glance. The edges between three adjacent bubbles, i.e., the liquid veins consisting of three Plateau's borders, have a shape nearer to a cylinder than to a flat slit. A fraction of the liquid descending in a foam passes inside the thin lamellae while the rest moves with the just mentioned liquid veins. The relative importance of these two fractions has not been studied. If the driving pressure is identical in both cases, the first fraction would be proportional to $L\delta^3/12$, if L is the width of lamella between two Plateau's borders, i.e., approximately the diameter of the bubble, and the second to $\pi r^4/8$, r being the radius of the liquid vein. The flow along the veins is more important than the flow inside the lamellae if $r > \delta(2L/3\pi\delta)^{1/4}$. If, for example, L/δ is 10,000, r must be greater than 1.2δ. This condition is likely to be satisfied by many foams.

Whatever the shape of the capillary space along which the liquid drains, the linear velocity of drainage should be proportional to the square of the smallest dimension of this space and inversely proportional to viscosity. Brady and Ross demonstrated that k in equation (11) was inversely proportional to viscosity when seven lubricating oils were compared at several temperatures. However, no convincing proof could be adduced for the identity of δ or r in all these foams (see also section 60).

Section 57. The progress of drainage in a horizontal film, in which the suction by Plateau's border is the only driving agent, can be calculated if this suction (P_c dynes/cm^2; the subscript c is for capillary) does not vary during the thinning of the film, i.e., if the radius of curvature of the border is independent of film thickness. If the center of a circular liquid plate is subjected to pressure zero while the pressure around the edge of the plate is $-P_c$, then

$$\frac{1}{\delta_2^2} - \frac{1}{\delta_1^2} = \frac{4P_c t}{3\eta a^2} \tag{19}$$

(see, e.g., ref. 19). In this equation t is time required for the film thickness to diminish from δ_1 to δ_2, a is the radius of the plate, and η the viscosity of the liquid. Film thickness decreases from δ_1 to δ_2

when the liquid volume $V = \pi a^2(\delta_1 - \delta_2)$ has flowed away. Hence, the relative amount of drainage is

$$\frac{V}{V_0} = 1 - \frac{1}{\left(\frac{4tP_c}{3\eta a^2}\,\delta_1^2 + 1\right)^{1/2}} \tag{20}$$

If two foams are compared after time t, the relative loss of liquid is greater the greater the ratio $P_c\delta_1^2/3\eta a^2$, i.e., not only the thicker the film but also the smaller its area.

Section 58. There are no data on the rate of drainage available for simple systems such as aqueous alcohols, as the lifetime of their foams is too short.

For *soaps* it was found that the "foam number" after 3 minutes (see section 54) increased from sodium linoleate to sodium stearate to sodium palmitate to sodium oleate to sodium laurate and had the greatest value for sodium myristate. Potassium soaps had greater "foam numbers" than sodium soaps. Sodium chloride and glycerol retarded the drainage of these foams[20]. It can be interpolated from the values reported by Merril and Moffett[7] that the time T_1 for half the liquid in the foam to drain was about 90 sec for 0.1 per cent (impure) sodium oleate and about 20 sec for 0.1 per cent sodium laurate, i.e., the drainage was less rapid in oleate solutions, contrary to the observations by Godbole and Sadgopal.

For a commercial soap, T_1 rapidly increased with concentration. When the solution contained 0.1, 0.2, and 0.4 per cent fatty acid (as soap), T_1 was 11 sec, 30 sec, and 105 sec, respectively[21]. The "foam power" (section 54) of three commercial soaps in 0.1 per cent solutions was 70 to 80 when the solutions had no prolonged contact with air. The numbers were 10 to 30 after storing in air for a day or two[5]. When 50 cm^3 of a solution containing 0.12 per cent fatty acids (as soap) was shaken and allowed to drain, the volume of liquid remaining in the foam was after 1 min. 24 to 33 cm^3 when the solution was kept in a closed vessel, and 10 to 12 cm^3 after the solution was open to air for 12 hours; after 5 min. the corresponding volumes were 15 and 4 cm^3, respectively[22].

Equation (11) (section 55), was not valid for the drainage of either soaps[7, 22] or *synthetic detergents*[7]. Ross, however, observed[16] that when the bubbling used to produce foam is slow, the major part of the

drainage curve (V against t) conforms to this equation; only at the beginning is the drainage too rapid and at the end too slow. This was the case for 0.025 to 0.1 per cent solutions of sodium bis(α-ethylhexyl) sulfosuccinate and 0.1 to 0.4 per cent solutions of dodecanesulfonic acid. The values of k were, for example, 0.005 sec^{-1} for 0.1 per cent of the sulfosuccinate and 0.004 sec^{-1} for 0.1 per cent sulfonic acid. Sodium lauryl sulfate foams seem to drain more slowly. It appears from the drainage curve of 0.2 per cent solution that k would be about 0.001 sec^{-1} in this instance[23]. Also this foam was made by bubbling. Analogous tests on the sodium salts of the sulfates of the other dodecanols showed that the 2-dodecanol derivative drained more rapidly than the sodium lauryl sulfate (which belongs to 1-dodecanol), while the derivatives of 3-, 4-, 5-, and 6-dodecanol had an even greater rate of drainage, almost identical for these four isomers. The rate of drainage of 0.2 per cent sodium lauryl sulfate solution was smaller also than those of 0.2 per cent solutions of dodecylamine hydrochloride, N,N-diethyldodecylamine hydrochloride and N,N-diethanoldodecylamine hydrochloride; the curves for these three salts were almost coincident.

Values found for the rate of drainage of synthetic detergents overlap those valid for soaps. Thus the time required for 40 cm^3 liquid to exude from a foam column containing 70 cm^3 liquid was 27 sec for sodium laurate, 96 sec for technical sodium octadecenyl sulfate, 122 sec for (impure) sodium oleate, 131 sec for sodium bis(α-ethylhexyl) sulfosuccinate, and 138 sec for a sodium "alkyl arylsulfonate," all in 0.1 per cent solution[7].

Section 59. The work by Arbuzov and Grebenshchikov on drainage of *saponin* foams was discussed in section 55. The considerable acceleration of drainage caused by tenfold dilution, as observed by these authors, was not confirmed by Gray and Stone[24] who found k in equation (11) to be about 0.0035 to 0.004 sec^{-1} for all solutions between 0.1 and 2 per cent. The concentration dependence is not very marked also in more dilute solutions[2]. Thus the percentage of liquid remaining in the foam after 1 min. was 40 per cent in 0.1 per cent and 19 per cent in 0.01 per cent digitonin solution. In 0.1 per cent solution this percentage little depended on the nature of saponin but, for example, in 0.02 per cent solution is decreased from guaiac

saponin to digitonin to commercial saponin to cyclamin to quillaja saponin[2].

Not only the absolute rate but also the relative rate of drainage of 0.1 per cent saponin solution increased with the wetness of the foam. A foam containing 3.2 cm^3 liquid in 100 cm^3 lost half its water within 30 min., while the separation of half the liquid from a foam containing 13 cm^3 liquid in 100 cm^3 required less than 9 min.[25]. Such behavior is consistent with the theories discussed in section 56. The rate of drainage of 0.4 per cent saponin foam was not altered by placing the foam under the pressure of 100 cm of mercury[26].

Constant k calculated on assumption of the validity of equation (11) was almost independent of concentration (0.1 to 2 per cent) also for egg albumin (k was about 0.0055 sec^{-1}) and peptone (k was 0.01 approximately); it increased with concentration in the just mentioned interval from 0.01 to 0.017 sec^{-1} in the instance of gelatin[24].

Data exist on the drainage of foams of alkaline lignin solutions[12] and of soaps made from the sulfate liquor of wood pulp manufacture[27].

Section 60. Equation (11) was found valid for beer foam[10] and was used without proof also for wine foam[28]. The drainage of wine is more rapid (k is, for example, 0.03 sec^{-1}) than that of beer whose k is 0.009 to 0.010 sec^{-1} [24] or 0.003 sec^{-1} [3].

These values were observed when the gas bubbling through beer was carbon dioxide. The rate of drainage was less when other gases were used. Thus constant k in the instance of nitrogen was one-quarter that in the instance of carbon dioxide[10]. According to Helm and Richardt[3] the ratios of k for CO_2, H_2, O_2, N_2, and air were 1:0.41:0.34:0.28:0.27. The authors point out that the order of gases in this series is almost identical with that of the product (coefficient of diffusion $\times$ solubility) of the gas (see also section 66). In other words: the more rapid the transfer of gas across foam films the greater the rate of drainage. In a simpler system this rule would be a decisive argument for the statement that the liquid exuded originates chiefly from ruptured bubbles (as distinct from drainage proper) since different gases are not likely to influence the values represented in the right-hand term of equation (17), section 56, or equation (20), section 57. However such a statement would not be warranted in a liquid as little understood as beer. Drainage of beer is retarded, for example,

by gum arabic and albumin and accelerated by filtration[29]; this can be accounted for by the effect of additions on viscosity η in the just mentioned equations. The rate of drainage of beer is greater at 20° than at 10°; this also would agree with the above equations as viscosity of beer decreases with increasing temperature. The "total head" of beer (section 54) is a linear function of its content of carbon dioxide[3].

Drainage of egg white foam produced with a kitchen mixer was smaller when the viscosity of the liquid exuded was greater[9]. However the product of dV/dt and η was not constant. For example, dV/dt was augmented fivefold when η decreased in the ratio 1:0.56. According to section 56, dV/dt should rapidly increase with the thickness of the films in which drainage takes place. The experimental results seem to contradict this expectation. The density of the foams was gradually reduced by continuous whipping; thus it was, for example, 0.14 g/cm^3 after 1 min. and 0.10 g/cm^3 after 5 min. beating. Lighter foams contain less liquid and might be expected to consist of thinner films; however drainage was more rapid in these systems. Perhaps the observation that foams beaten for a longer time were made up of smaller bubbles supplies the explanation. If there are more bubbles, there are more liquid veins in Plateau's borders; and if the bubbles are smaller, the distance between the nearest Plateau's borders is smaller; the first factor would widen the path open to the draining liquid and the second factor would enhance the force driving it. If drainage proceeded along the films rather than veins, equation (20) might account for Barmore's observations. In less dense foams δ_1 was smaller, but a (i.e., bubble radius) was smaller still, thus making the ratio δ_1^2/a^2 greater than for denser foams. This, in accord with (20), implies a greater ratio V/V_0.

Among *nonaqueous liquids*, lubricants[13] and vegetable and animal oils have been studied. The half-life T_1 (section 55) of oils ranged from 53 min. for a lecithin-containing soybean oil and a chestnut oil to less than 3 min. for hayfish oil; the foam was made by bubbling[6]. Purification of oil reduced T_1, and addition of lecithin extended it. Different gases were compared using a sample of linseed oil, and T_1 was found to be 36, 36, 31, and 22 min. for air, nitrogen, hydrogen, and carbon dioxide, respectively. As in the instance of beer, the rate of drainage increased from nitrogen to hydrogen to carbon dioxide, although the differences were less marked. Also in the instance of oils it is not known why the nature of the gas is so important.

Section 61. Very little is known concerning the relation between persistence of a foam and its experimental rate of drainage. As mentioned in section 53, a definite relation cannot be expected as long as the measured drainage is "pure drainage," not complicated by rupture of the bubble walls. In particular when the rate of drainage is determined above all by the viscosity of the descending liquid, persistence will not go hand-in-hand with the time of retention of liquid in the foam.

Lederer[21] compared the time of collapse t_1 (section 29) and the half-time of drainage T_1 of foams produced by bubbling air through solutions of commercial detergents and soaps. In all instances t_1 was much greater than T_1. For example, for the three soap solutions mentioned in section 58, t_1 was longer than 4 hours while T_1 was 11 to 105 sec. There was no definite ratio between t_1 and T_1, and the order of solutions according to increasing values of T_1 was different from the series arranged according to increasing t_1 values. For instance, T_1 was 12 sec for both 0.05 and 1 per cent solutions of "Igepon A" (a synthetic detergent) while the corresponding t_1 were 0.5 and 2 hours, respectively.

The most persistent bubble (see sections 19 and 38) of 0.1 per cent (impure) sodium oleate existed for as many seconds as were required for 25 per cent of the liquid to drain[7]. This, of course, would be impossible if in both procedures equal foam volumes were compared. Actually, however, the amount of foam used for persistence measurements was a small fraction (presumably less than 1 per cent) of the amount employed for drainage. It is unknown whether this fraction was constant for different solutions or was one of the reasons for the great divergence of the following figures. The bubble persistences corresponded to the following percentages of liquid exuded: about 75 per cent for 0.1 per cent sodium laurate, about 23 per cent for 0.1 per cent sodium bis(α-ethylhexyl) sulfosuccinate, 57 per cent for 0.1 per cent technical sodium octadecenyl sulfate, about 53 per cent for 0.1 per cent commercial sodium "alkyl aryl sulfonate," etc. Thus there is no quantitative correlation between persistence and rate of drainage. If any qualitative correlation exists, it seems to be such that more slowly draining foams have greater lifetimes.

No definite correlation was found between Stiepel's "foam number" (section 54) on one hand and the height of foam produced by shaking or moving a perforated plate (section 25) on the other hand. The liquids used were solutions of commercial detergents[30].

The magnitudes L_g and L_l (see sections 28 and 55) have been compared for several systems[13]. In a lubricating oil, which also otherwise showed an unusual behavior, the average lifetime of gas in the foam was shorter than the average lifetime of liquid, i.e., liquid seemed to be present in foam also when there was no foam left. In all other instances, however, L_g was larger than L_l, i.e., bubbles persisted also after a considerable portion of the liquid making up their walls had oozed away. In lubricating oils the ratio L_g/L_l usually was less than two, but in a sample of beer it was 7.5. It was mentioned in section 56 that k (and consequently also L_l) of lubricating oils was a function of their viscosities. As would be expected no such correlation existed for L_g. At a given viscosity, i.e., at different temperatures, the values of L_g were different for different oils.

A third solute differently affects L_l and L_g of a solution of two compounds[31]. Several additions were made to an aqueous solution of a commercial detergent ("Nacconol NRSF") and sodium silicate. Tributyl phosphate was the second best depressor of foam if L_l was considered, but was the 6th in its effect on L_g. On the contrary, 4-methyl-2-pentanol was the second best depressor as far as L_g was concerned but occupied the fourth place in respect to L_l. In other words, methylpentanol destroyed foam when this was still very "wet" while tributyl phosphate hastened draining of the foam which then collapsed after reaching a relatively dry state.

References

1. Stiepel, C., *Seifensieder-Ztg.*, **41**, 347 (1914).
2. Sieburg, E., and Bachmann, F., *Biochem. Z.*, **126**, 130 (1922).
3. Helm, E., and Richardt, O. C., *J. Inst. Brewing*, **42**, 191 (1936).
3a. Brenner, M. W., McCully, R. E., and Laufer, S., *Am. Brewer*, **84** (2) 39, 49 (1951).
4. Bailey, M. I., *Ind. Eng. Chem.*, **27**, 973 (1935).
5. Preston, W. C., and Richardson, A. S., *J. Phys. Chem.*, **33**, 1142 (1929).
6. Kaufmann, H. P., and Kirsch, P., *Fette u. Seifen*, **47**, 196 (1940).
7. Merrill, R. C., and Moffett, F. T., *Oil & Soap*, **21**, 170 (1944).
8. Arbuzov, K. N., and Grebenshchikov, B. N., *J. Phys. Chem. (U.S.S.R.)*, **10**, 32 (1937).
9. Barmore, M. A., *Colo. Agr. Expt. Sta., Tech. Bull.* **9**, (1934).
10. Blom, J., *J. Inst. Brewing*, **43**, 251 (1937).
11. Clark, G. L., and Ross, S., *Ind. Eng. Chem.*, **32**, 1594 (1940).
12. Erbring, C., and Peter, H., *Kolloid-Z.*, **96**, 47 (1941).
13. Brady, A. P., and Ross, S., *J. Am. Chem. Soc.*, **66**, 1348 (1944).
14. Lederer, E. L., *Seifensieder-Ztg.*, **63**, 331 (1936).
15. Miles, G. D., Shedlovsky, L., and Ross, J., *J. Phys. Chem.*, **49**, 93 (1945).

16. Ross, S., *J. Phys. Chem.*, **47**, 266 (1943).
17. Plateau, J., *Mém. acad. roy. sci. Belgique*, **37** (1869). 8th ser.
18. Gibbs, J. W., "The Collected Works," Vol. I, p. 307, New York, Longmans, Green & Co., 1928.
19. Bikerman, J. J., "Surface Chemistry for Industrial Research," p. 359, New York, Academic Press, Inc., 1948.
20. Godbole, N. N., and Sadgopal, *Kolloid-Z.*, **75**, 193 (1936).
21. Lederer, E. L., *Angew. Chem.*, **47**, 119 (1934).
22. Hetzer, *Chem. Ztg.*, **72**, 715 (1932).
23. Padgett, A. R., and Degering, E. F., *Ind. Eng. Chem.*, **32**, 486 (1940).
24. Gray, P. P., and Stone, I., *Wallerstein Labs. Communs.*, **3**, 159 (1940).
25. Siehr, A., *Kolloid-Z.*, **77**, 27 (1936).
26. Siehr, A., *Kolloid-Z.*, **78**, 156 (1937).
27. Elkonin, N. V., *Bumazh. Prom.*, **19** (2), 21 (1941); *Chem. Abs.*, **38**, 2819 (1944).
28. Amerine, M. A., Martini, L. P., and De Mattei, W., *Ind. Eng. Chem.*, **34**, 152 (1942).
29. Schwarz, R., and Laufer, S., *Amer. Brewer*, **70** (12), 30 (1937).
30. Raison, M., and Matalon, R., *Mém. services chim. état (Paris)*, **34**, 353 (1948).
31. Ross, S., and Young, G. J., *Ind. Eng. Chem.*, **43**, 2520 (1951).

5. MECHANICAL PROPERTIES OF FOAMS

Section 62. *Density* was measured more often than any other mechanical property of foams. If the foam is sufficiently stable, density is measured by filling a tared vessel of known capacity with the froth and weighing. Let the weights of the empty and the filled vessel be W_0 and W_1, respectively, and the capacity be V_0; the foam density then is

$$[\rho] = \frac{W_1 - W_0}{V_0} \tag{21}$$

This method has been used, for example, for foams of egg white[1, 2, 3] and of paper coating compositions[4]. If the foam is made by bubbling a gas through volume V_1 of liquid, the foam volume is V_2, and the liquid volume (during bubbling or immediately after its cessation) is V_3, then

$$[\rho] = \frac{\rho(V_1 - V_3)}{V_2}, \tag{22}$$

ρ being the density of the liquid in the foam. Sometimes V_3 has to be corrected for the volume of gas bubbles still present in the liquid. Equation (22) assumes that the specific gravity of the gas within the foam bubbles is equal to that of the ambiant air. This assumption is obviously incorrect when a gas different from air is used for bubbling, but it is not exact also when air is employed as the gas phase of a foam is compressed and has higher density than the outside air (see section 64). However, these errors may be neglected for, and equation (22) applied to, all customary foams.

Often instead of density a related quantity is calculated. As follows, for example, from equation (22), the ratio $[\rho]/\rho$ is equal to the ratio "volume of liquid in foam : volume of foam." It was determined, for example, by Gray and Stone[5]. The inverse ratio $\rho/[\rho]$ is termed "expansion factor"; it was calculated, for example, by Clark[6]. The function $100\left(\frac{\rho}{[\rho]} - 1\right)$ was defined as "increase in volume on foam-

ing" or "foaming power."[3] In a foam whose $[\rho]$ is, say, 0.104 g/cm^3 and $\rho = 1.04$ g/cm^3, 0.1 of the volume is liquid, 0.9 of the volume is gas, and $100\left(\frac{\rho}{[\rho]} - 1\right) = 900$.

To render the part played by the solute more conspicuous, the volume of foam may be compared with the volume (or mass) of solute in it rather than with the volume of solution[1]. Thus if a grams of a frother were dissolved to make V_1 cm^3 solution and this solution was converted into V_2 cm^3 foam, V_2/a is the foam volume produced by 1 g solute (see also section 24).

Section 63. Foam densities may range from almost zero to, say, $\rho/2$. The low values would be observed when the vessel (see equation (21)) contains but one or few foam films. Let the vessel have the capacity of 100 cm^3, the total area of the films in it be 100 cm^2, and the film thickness be 10^{-5} cm; then $[\rho]$ would be approximately 10^{-5} g/cm^3. The upper limit is determined by what we choose to call foam as distinct from an emulsion of gas in liquid (see section 1). If we specify, for example, that in a foam the gas phase should occupy at least half the volume, then the greatest possible foam density is $\rho/2$.

It is clear from equation (22) that during drainage and collapse of a foam, $[\rho]$ decreases in time if the rate of drainage exceeds the rate of collapse, i.e., if $V_1 - V_3$ decreased more rapidly than V_2. If the collapse is the more rapid process, $[\rho]$ gradually increases. Both effects have been observed in foams of heptanoic acid in water[7]. In more concentrated solutions, $[\rho]$ rose and in dilute solutions diminished during the course of collapse.

Most density measurements have been carried out on very stable foams.

The ratio $[\rho]/\rho$ was roughly 0.2 for the solutions of a commercial alkyl sulfate detergent as long as its concentration was between 0.2 and 2 per cent, but in a 0.05 per cent solution this ratio was near 0.13[5]. For saponin solutions between 0.2 and 2 per cent, $[\rho]/\rho$ was approximately 0.22 but it decreased to 0.08 in about 0.05 per cent solution. Gum arabic had $[\rho]/\rho$ of 0.04 in 1 per cent and 0.20 in 2 per cent solution. Peptone and gelatin had $[\rho]/\rho$ of 0.16 to 0.20 between 0.2 and 2 per cent, but approximately 0.05 per cent solutions showed $[\rho]/\rho$ as low as 0.03. All the foams mentioned in this paragraph were produced by bubbling carbon dioxide through the solutions[5].

By varying the conditions of bubbling, $[\rho]/\rho$ of 0.1 per cent saponin foams could be varied, for example, between 0.03 and 0.13[8].

Several measurements have been reported on the density of foams of egg white and egg albumin. Whipped egg white foams may have densities between 0.15 and 0.19 g/cm^3 depending on the speed and duration of whipping[1], 0.14 to 0.10 g/cm^3 after different whipping times ($[\rho]$ decreasing on prolonged beating)[2], 0.21 to 0.09 g/cm^3 according to the mixing machine used[3], and so on. Dilution with water had but little effect on $[\rho]$ as long as the mixture contained more than 60 per cent of egg white, but $[\rho]$ of mixtures containing 20 per cent egg white and 80 per cent water was about 0.25 as against 0.15 of undiluted specimens[1]. However, ratio $[\rho]/\rho$ in pneumatic foams of egg albumin gradually increased from 0.04 at 0.08 per cent to 0.15 at 0.5 per cent and 2 per cent[5]. The effect of alkalinity on $[\rho]$ of egg white seems to be different for fresh and stored eggs. The $[\rho]$ of egg white foam was doubled by about 0.7 per cent cottonseed oil[1] or by about 0.15 per cent olive oil[3]. The addition of olive oil increased the volume exuded within 1 hour by about 15 per cent. Increase of *rate* of drainage with density is in accord with the theories of section 56. However, egg yolk, added in comparable amounts, increased both foam density and the *time* of drainage. The bubble size was not determined (see section 60). The density of foam produced by beating whole egg powder with 1.8 parts of water was not affected by whey solids or lactose, but addition of 0.4 part sucrose lowered $[\rho]/\rho$ from 0.24 to 0.15[9]. Small additions of commercial detergents (up to 0.5 per cent) increased $[\rho]/\rho$ (up to 20 per cent)[9].

The ratio $[\rho]/\rho$ of beer foam produced by introduction of carbon dioxide was 0.20 to 0.23 for four different samples of beer. Dilution lowered this ratio until it was 0.04 to 0.13 for beer plus 9 parts of water[5]. Beer containing more carbon dioxide gave, on sudden lowering of pressure, a less dense foam than less carbonated beer[9a].

Rather dense foams have been obtained by shaking solutions of commercial detergents in viscous organic liquids. Thus, 1 per cent solution of an N-acyl-N,N′,N′-tris(hydroxyethyl) ethylenediamine hydrate in glycerol had $[\rho]$ of 0.30 g/cm^3; 1 per cent solution of a sodium "aryl sulfonate" in glycerol had $[\rho] = 0.48$; and 0.5 and 1 per cent solutions of a polyethylene glycol in glycol showed foam densities of 0.17 and 0.12 g/cm^3, respectively[10].

Ten lubricating oils, whose foams had persistences (L_g, see section 28) ranging from 18 to 4920 min., gave whipped foams in which

the densities were confined between 0.39 and 0.62 g/cm^3. These systems would be called emulsions rather than foams (see above). The difference between the wide range of persistences and the narrow range of densities is striking[11].

The high values of foam density mentioned above may give an erroneous idea of the thickness of foam lamellae. If, as a first approximation, foam is pictured as consisting of cubes with edges of l cm, each cube containing l_0^3 cm^3 of air, then the thickness of each lamella is $l - l_0$ cm. The ratio $[\rho]/\rho$ (or of liquid volume to total volume) in such a foam is $(l^3 - l_0^3)/l^3$. If this ratio is 0.5, then $l - l_0 = 0.21\ l$, i.e., at $[\rho]/\rho$ as great as 0.5 the thickness of the lamellae is only 21 per cent of the cube edge. At $[\rho]/\rho$ equal to 0.3, 0.2, and 0.1, the lamella thickness is 11, 7, and 3 per cent, respectively, of the cube edge.

Section 64. The *size of bubbles* in a foam can be selected at will, within limits (see sections 3–6). It affects the lifetime of a foam (see section 19). It is said that when persistence increases with concentration of the solute, the bubble size decreases at the same time[12].

The bubble size influences also the *gas pressure* in a foam. If a bubble is separated from atmosphere by a lamella whose radius of curvature is R_1, the gas pressure in the bubble is by $4\gamma/R_1$ dynes/cm^2 greater than the atmospheric pressure (see section 15). If, for example, surface tension γ is 40 g/sec^2, the pressure difference P_c (see section 57) is 160 dynes/cm^2 at $R_1 = 1$ cm and 1,600 dynes/cm^2 at $R_1 = 0.1$ cm. As atmospheric pressure is about 10^6 dynes/cm^2, it is clear that the internal pressure in foams is not very different from the external pressure.

P_c has been measured in the apparatus shown in Fig. 12, section 21. A foam column was built up by bubbling; then the air current was turned off and stopcock 9 closed. Gage 6 first registered atmospheric pressure in the measuring tube, but the pressure increased as long as the foam was collapsing, and pressure difference reached values as high as 3 cm of water, i.e., about 3,000 dynes/cm^2, for 0.001 M solution of *o*-cresol[13]. Assuming γ to be 60 g/sec^2 this would indicate bubble diameter of approximately 0.16 cm. However, the visible bubbles were considerably bigger[14] (see also section 69).

Section 65. Since internal pressure in a foam is greater than the atmospheric, the *compressibility* of foam should correspond to that of

a slightly compressed gas rather than to that of a gas at atmospheric pressure, even if the effect caused by surface deformation is neglected. Unfortunately the experiment on compressibility of foam described in the literature was not sufficiently comprehensive to test this conclusion. Potato juice diluted with 1 part of water (it then contained 0.3 per cent protein) was converted into foam, and this was introduced into a tube, closed at one end, to the 100 cm^3 mark[15]. Then the space above the foam was connected with compressed air, and the foam volume was read at different excess pressures. It was, for example, 90 cm^3 at the pressure difference of 94 mm Hg, 81 cm^3 at 180 mm, and 69 cm^3 at 360 mm. Hundred cm^3 of a perfect gas under 800 mm Hg would be compressed by 94 mm Hg to 90 cm^3, by 180 mm Hg to 82 cm^3 and by 360 mm Hg to 69 cm^3. Thus foam behaved as perfect gas at 800 mm Hg pressure. No mention of the initial pressure could be found in Siehr's paper, and it is not known whether the calculated pressure of 800 mm Hg corresponded to any physical reality (see also below).

Deryagin[16] pointed out that compressibility of foam should be different from that of the gas phase in the foam because compression deforms the lamellae also. Deryagin's result can be obtained, for example, by the following reasoning. The external pressure P_e equals $P_i - P_c$, P_i being the internal pressure, and P_c the capillary pressure. Hence

$$\frac{dP_e}{dv} = \frac{dP_i}{dv} - \frac{dP_c}{dv}, \tag{23}$$

if v is foam volume and the liquid part of this volume is neglected. In a perfect gas

$$\frac{dP_i}{dv} = -\frac{P_i}{v} \tag{24}$$

The capillary pressure is inversely proportional to bubble radius R_1, i.e., is $kv^{-1/3}$, k being a constant. This yields

$$-\frac{dP_c}{dv} = \frac{P_c}{3v} \tag{25}$$

Introducing (24) and (25) into (23) yields

$$\frac{dP_e}{dv} = -\frac{P_i}{v} + \frac{P_c}{3v}$$

and

$$-\frac{vdP_e}{dv} = P_i - \frac{P_c}{3} = P_e + \tfrac{2}{3}(P_c) = \tfrac{1}{3}(P_e + 2P_i) \tag{26}$$

As compressibility is always referred to external pressure, the expression $-\frac{vdP_e}{dv}$ is the inverse value of the compressibility of foam. Its magnitude depends not only on the internal pressure P_i, as would be the case in the absence of film deformation, but also on surface tension and bubble size which determined the value of P_c. It is true that correction term $P_c/3$ usually will be but a small fraction of the main term P_i. Instead of Boyle's law the volume and external pressure on a foam would be related by equation

$$\left(P_e + \frac{a\gamma}{v^{1/3}}\right)v = RT \tag{27}$$

in which a is a constant depending on the shape of the foam cells[16]. R is the gas constant, and T is absolute temperature.

Deryagin's theory neglects the liquid volume in the foam. The presence of (virtually incompressible) liquid presumably affects the value of compressibility more than the correction factor occurring in equation (26). If the foam volume v consists of gas volume v_1 and liquid volume v_2, then $dv/dP_e = dv_1/dP_e$, but the compressibility

$$-\frac{dv}{vdP_e} = \frac{v_1}{v_1 + v_2} \cdot \frac{1}{P_e} \tag{28}$$

rather than $-\frac{dv}{vdP_e} = \frac{1}{P_e}$ as would be in a perfect gas containing no liquid. Suppose one-tenth of the foam volume is liquid (see section 63). Then $(v_1 + v_2)/v_1 = 1.11$, and foam under a pressure P_e would behave as if its pressure were 1.11 P_e. This may be the explanation of the small compressibility observed by Siehr.

Section 66. It is implied in section 65 that capillary pressure inside a foam has one definite value. This is true only if all the bubbles are equal in size. If, as usual, the foam is polydisperse (i.e., consists of bubbles of different sizes), capillary pressure is different in different bubbles and causes diffusion of gas from smaller to greater bubbles.

Let the radius of the smaller bubble be R_1 and that of the larger

bubble R_2. The area of the septum between the bubbles (see section 15) will be approximately proportional to R_1^2. Then the amount of gas diffusing through the septum in unit time (t) is

$$\frac{dM}{dt} = k_1 R_1^2 \gamma \left(\frac{1}{R_1} - \frac{1}{R_2} \right) \tag{29}$$

The constant k_1 will be proportional to solubility and diffusion coefficient of the gas in the septum and (approximately) inversely proportional to the thickness of the septum. The pressure difference causing the diffusion is $\frac{4\gamma}{R_1} - \frac{4\gamma}{R_2}$. Mass M_1 of gas in the smaller bubble is proportional to the volume of the bubble if capillary pressure is neglected in comparison with the atmospheric pressure. Hence $M_1 = k_2 R_1^3$, k_2 being a factor which does not vary during the diffusion. As $-dM_1/dt = dM/dt$, equation (29) becomes $3k_2 R_1^2 \frac{dR_1}{dt} = -k_1 R_1^2 \gamma \left(\frac{1}{R_1} - \frac{1}{R_2} \right)$ or

$$\frac{dR_1}{dt} = -k_3 \gamma \left(\frac{1}{R_1} - \frac{1}{R_2} \right) \tag{30}$$

if k_3 is used as abbreviation for $k_1/3k_2$. Thus the rate of decrease of the bubble radius is proportional to the difference of the curvatures. The capillary pressure in a bubble has been measured as early as 1861[17] and 1866[18], but an equation analogous to (30) was first deduced apparently by Dewar[19].

If there is only one bubble, then $(1/R_2) = 0$ and integration of the resulting equation $dR_1/dt = -k_3\gamma/R_1$ yields

$$R_0^2 - R_1^2 = 2k_3\gamma t, \tag{31}$$

if R_0 is the initial radius of the bubble, i.e., at time $t = 0$. Equation (31) was confirmed in two instances (not completely specified) but in many other instances it was not valid[19]. Dewar attributed this to chemical change of the bubble wall (a soap solution in aqueous glycerol) causing a change in γ, but alteration of the wall thickness affecting the value of k_3 is at least as likely. The contraction of a bubble was more rapid the smaller the pressure outside the bubble (and of course also inside the bubble as the latter was by $4\gamma/R_1$ greater than the former). This would be expected as the amount diffused through a septum depends chiefly on the pressure difference (i.e., $4\gamma/R_1$) while the volume occupied by a given amount of gas is

inversely proportional to the pressure. Or, in mathematical language, dR_1/dt is greater at small pressures because k_3 is greater (k_2 is smaller) than at greater pressures. A bubble, 14 cm in diameter, of 3 per cent ammonium oleate in 30 per cent glycerol contracted in 15 min. to 12 cm at 5 mm Hg air pressure and to 4 cm at 1 mm Hg[19]. Contraction of soap bubbles filled with hydrogen at pressures above the atmospheric also has been observed[20]. As gas diffusion through thicker septa takes more time, thick bubbles contracted more slowly than thin ones; e.g., the contraction from 10 cm to 6 cm diameter required 45 hours when the bubble was "almost too thick to show color" and only 9 hours when it was of "intense green" color[19].

The variation of disperity in foams containing many cells also has been examined[21]. Some of the results thus obtained are mentioned in section 50. The "specific surface" decreased, i.e., the average bubble size increased for carbon dioxide foams more rapidly than for oxygen or air foams. This is in qualitative agreement with equation (29). Constant k_1 in it should be proportional to solubility and to rate of diffusion. As the product of solubility (cm^3 of gas in cm^3 of liquid) and diffusion coefficient (cm^2/sec) is for carbon dioxide 0.9×1.8, i.e., 1.6, and for oxygen 0.03×2, i.e., 0.06, the more rapid transport of carbon dioxide is accounted for (see also section 60). When a definite cluster of bubbles (air in an aqueous dispersion of "ferrous protein hydrolyzate") was observed at regular time intervals, all bubbles greater than 0.007 cm in diameter were seen to expand, all bubbles smaller than 0.005 cm shrank, and the bubbles in the intermediate region of diameters had no consistent behavior. The shape of the curves "bubble diameter versus time" was too variable to be fitted by any theory.

Since larger particles grow and smaller particles shrink, aged foams should be more polydisperse than fresh foams. The truth of this conclusion is exemplified in Fig. 33 from Clark and Blackman[21]. The mean diameter d of the bubbles (except those smaller than 0.005 cm) is plotted along the abscissa. The ordinate, instead of the number n of the bubbles of the specified size, represents the "specific surface" of these bubbles, i.e., a value proportional to nd^2. Thus, line marked 8 which is almost parallel to the abscissa means that the number of bubbles was approximately inversely proportional to d^2. The numbers at the curves refer to foam age in minutes. It is seen that the spread of nd^2 values increased with age. The liquid employed was 5 per cent soap dispersion.

In a froth column the average bubble size may differ at different levels. Fig. 34, from Mit'kevich[22], shows that the diameter of bubbles 9.5 cm above the base of the column was greater than that at the 6 cm level and remained greater during the coarsening of the foam.

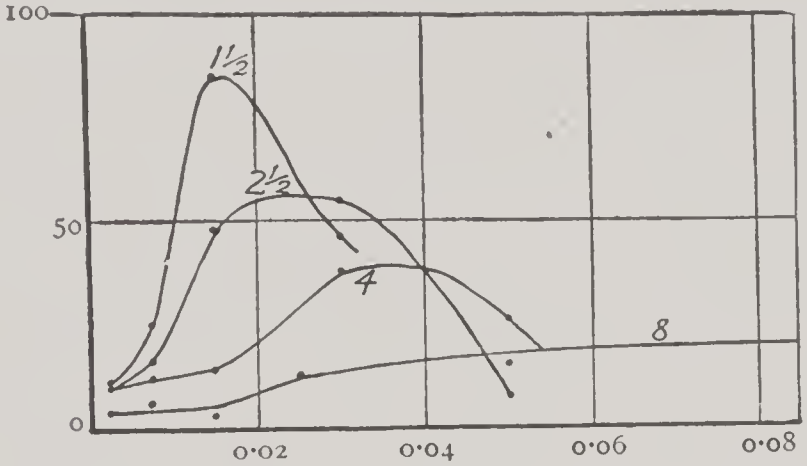


FIGURE 33. Increase in polydispersity of foam of 5% soap dispersion. Abscissa: bubble diameter d, in cm. Ordinate: πnd^2, n being the number of bubbles, having diameteres near d, in unit volume of foam. The curves refer to 1.5, 2.5, 4, and 8 minutes old foams. From *Trans. Faraday Soc.*, **44**, 1 (1948).

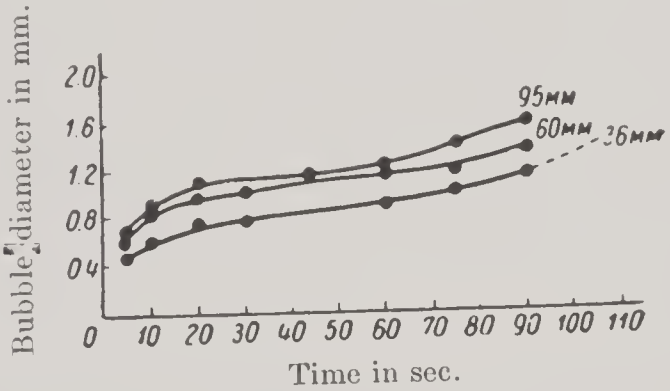


FIGURE 34. Growth of bubbles in the foam of 0.25 per cent malt solution. Figures at the curves: height above the base of the foam column. From *J. Applied Chem.* (*U.S.S.R.*), **21**, 817 (1948).

Analogously, the bubbles at the 6 cm level were greater than those at the 3.6 cm level. The abscissa of the figure is time in seconds and the ordinate represents diameters in mm. The foaming liquid was 0.25 per cent malt solution, and the foam was produced by the pneumatic method (see section 21). When individual bubbles were followed during their rise through the foam column, it was seen that their diameter gradually increased. In one instance this was 0.04 cm at the bottom and 0.16 cm at the top of the column 90 sec. later.

Section 67. The *hydrostatic pressure* exerted by a foam column has been measured. In the "saturation" of beet sugar juice, carbon dioxide is bubbled through the juice contained in tall vessels. Bruckner (see Schiebl[23]) mounted in these vessels bells filled with air and connected with U-tubes containing water, which acted similarly to pressure gauges. The liquid level before "saturation" was at 160 cm. A gauge attached at the 80 cm level naturally registered pressure of 80 cm water. This pressure rose to 120 cm during the steady state of bubbling and foaming (on continued bubbling the foam collapsed and the pressure decayed almost to the initial value). The pressure at the 160 cm level naturally was zero before bubbling, but remained equal to 80 cm water during the steady frothing. Unfortunately the amount of liquid in the foam was not determined. Did, for example, the foam above the 160 cm mark contain liquid equivalent to an 80 cm layer?

For 0.01 to 0.1 per cent saponin solutions, the pressure shown by similar gauges was, as would be expected, greater the taller the foam column above the gauge and the denser the foam[8]. However, it was not proportional to the density. Thus for 0.05 per cent solution at a definite level the pressure was 3.2 cm of water for $[\rho] = 0.002$ and 4.8 cm of water for $[\rho] = 0.010$ g/cm^3 (see section 62). Apparently it depended also on the bore of the tube containing foam[8]. It is clear that at least a part of the weight of the foam is carried by the foam films attached to the walls: plugs of froth suspended in a tube are familiar formations. Hence, the hydrostatic pressure of a froth column is likely to be less than calculated from its weight.

Section 68. It is known that movement of a liquid-gas-solid boundary along a solid surface is subject to friction (for the most recent discussion see ref. 24). Similar effects are known for the movement of froth-gas-solid boundaries. Siehr[15] applied air pressure to one end of 1 meter long columns of potato juice foam, $[\rho] = 0.0098$ g/cm^3, until the opposite end started moving. The minimum pressure required was 93, 49, 29.5, and 26 cm of water when the tube (and column) diameter was 0.4, 0.8, 1.2, and 1.8 cm, respectively. Thus the minimum *pressure* (p) at a first approximation is inversely proportional to the tube diameter d, that is, the *force* ($\pi pd^2/4$) resisting the movement is proportional to the diameter (or also perimeter) of the tube. The force required to push a "pellet" or "index" of liquid

in a tube also is proportional to the perimeter of the cross section of the latter (i.e., to πd). The coefficient of proportionality ($\pi p d^2/4\pi d$) is of the order of magnitude of the surface tension of the liquid[24]. In the instance of the potato juice foam, however, this coefficient was for the narrowest tube 93 × 981 × 0.4/4, i.e., about 9,100 dynes/cm or g/sec^2, over 100 times as great as the surface tension of the juice. Perhaps over 100 films had to be displaced along the solid wall in Siehr's experiment while only two menisci move when a liquid "pellet" moves. Unfortunately the dependence of the excess pressure needed on the length of the foam column has not been investigated.

As would be expected, the pressure required to force a potato juice foam from a wide tube into a narrow one was greater the narrower the second tube[15].

Section 69. When foam is pushed in a tube, not only the resistance along the walls but also that in the body of the foam may be of importance. If this resistance is more or less independent of the rate of deformation, it may be expressed in terms of a shear modulus; otherwise, viscosity would be a more appropriate expression.

Deryagin[16] calculated the *shear modulus* of foam. An approximate equation can be gained by the following simplified reasoning. Imagine a slab of foam lying on an immobile solid plate and covered with another plate, l cm long. When to the upper plate shearing stress f is applied (f is force divided by the area of the plate) and this shifts the plate by l' cm, the modulus of elasticity in shear (or shear modulus) is $\mu = fl/l'$. We assume that the plate does not move further because the deformed foam films resist further deformation. Let the foam consist of bubbles of radius R. Then the number of bubbles in contact with 1 cm^2 of the upper plate is $1/\pi R^2$, and the total length of the films on this square centimeter is $2\pi R/\pi R^2 = 2/R$. Hence, surface tension γ acts on 1 cm^2 of the upper plate with the force $2\gamma/R$ which is equal to $P_c/2$ (see section 64). When stress is applied, only that component of this force resists it which is directed opposite to f. In others words, only the horizontal component of the surface tension of the deformed films is operative. For small values of l' this component may be assumed to be proportional to l', i.e., equal to $nl'\gamma$, n being a constant (its dimension is cm^{-1}). Then f becomes equal to

$P_c nl'/2$ and

$$\mu = {}^1{}_2 P_c nl. \tag{32}$$

Deryagin's formula is

$$\mu = 0.4 P_c \tag{33}$$

According to (33) the ratio of shear modulus to capillary pressure in a foam should be a constant independent of the extent of deformation, of the size and shape of the foam system, and of the physical properties of the foam. However, equation (33) has been tested in one apparatus only[25]. A circular plate was suspended on a metal ribbon so that it was partly immersed in a foam contained in a vessel. When the ribbon was twisted, the plate turned in its plane, and the resistance offered by the foam could be calculated from the experimental relation between the angle of rotation and the torque. Unfortunately, the equation used by the authors takes care of the deformation of the foam only between the plate and the vessel at the level of the plate and, apparently, neglects the deformation under the plate, which was considered in the preceding paragraph. No experiments to test this equation have been reported. For foams produced by whipping 0.002 per cent saponin solution, P_c values between 2900 and 10,100 dynes/cm^2 were found by measuring the increase in pressure caused by the collapse of the foam (see section 64). (If γ was 70 g/sec^2, the diameter of the bubbles in the last mentioned foam was 0.055 cm; no measurements are reported.) The shearing modulus μ was calculated to be 810 to 4,450 dynes/cm^2, and the ratio μ/P_c was said to be 0.23 to 0.70, i.e., near to the theoretical value of 0.4. On the other hand, in 0.1 per cent saponin foam P_c was 2700, μ was 22,000, and μ/P_c was 8.1. This great deviation from the theory is attributed[25] to the "elasticity" (or rather rigidity) of saponin films (see section 73) which resists their deformation more than surface tension does. New experiments would be highly welcome.

Section 70. Instead of a horizontal, a vertical plate suspended on a torsion wire can be used[6]. When such a plate hangs in a foam contained in a beaker, and the beaker is rotated at a constant rate (e.g., 8 revolutions per minute), the torsion of the wire first increases to a maximum and then decreases to a steady value. Under the assumption that shearing occurred along the cylindrical surface formed by the

vertical edges of the rotating plate, the maximum and the steady shearing stresses (S_1 and S_2) could be calculated. Hydrolyzed keratin gave the stiffest foam with S_1 of 350 and 2,250 dynes/cm^2 and S_2 of 230 and 1100 dynes/cm^2 in 1 and 10 per cent solutions, respectively. The values of S_1 and S_2 for soap foams apparently had maxima near 5 per cent concentration; both were then 320 dynes/cm^2. The foams were produced by beating with a perforated plate (see section 25). Both S_1 and S_2 increased with the rate of movement of the plate; the degree of dispersity of the foam increased simultaneously.

The stresses S_1 were found to be related to minimum stresses S_3 required to cause rotation of a disc lying in the surface of the solution (free from foam) and suspended on a torsion wire. For example, S_3 of 5 per cent hydrolyzed keratin solution was 3.11 dynes/cm. This value multiplied with the "specific surface" of the foam (see section 50) gave 410, 1,180, and 1,970 dynes/cm^2 for three foams prepared by beating at three different speeds. The stresses S_1 for these foams were 307, 937, and 1,180 dynes/cm^2, respectively, i.e., the ratio S_3/S_1 varied only between 1.3 and 1.9. If the liquid volume in the foam is small compared with the gas volume, the "specific surface" is approximately $2/R$, and the correlation found by Clark can be expressed as $S_1 = 2cS_3/R$, c being a factor between 1.3 and 1.9. From equation (33), $\mu = 1.6\ \gamma/R$. Presumably S_1 of Clark is closely related to μ of Deryagin and Obukhov.

Shearing of foam confined between two coaxial cylinders also was studied[25a]. The foam was produced by the pneumatic method and transferred into the annular space between two cylinders of which the external could be rotated while the internal was suspended on a torsion wire. When the external cylinder was turned by φ radians, the internal turned by $\varphi - \epsilon$ radians and the torque on it was P dynes/cm^2. The curves of P as function of ϵ (i.e., stress on foam as function of deformation) were of three types. In the first type P increased with ϵ to a maximum (e.g., of 10 dynes/cm^2 at $\epsilon = 0.2$), then decreased and finally became independent of ϵ (e.g., 5 dynes/cm^2 between 0.9 and 1.6 radians). The first increase of P with ϵ was linear; if along this stretch the external cylinder was stopped, ϵ and P remained constant until breakdown of the foam set in; thus at small ϵ these foams behaved as truly elastic bodies. At large ϵ perhaps slippage of foam at the internal surface occurred; because of this sliding the actual distortion of the foam was less than the value of ϵ would indicate, and, consequently, the value of P was smaller than

at smaller ϵ. Sodium salts of 6-butylnaphthalene-1-sulfonic acid, dioctyl succinosulfonic acid, and pyridineundecanesulfonic acid gave rise to such foams. In the second type P increased with ϵ to a plateau. Saponin solutions containing more than 0.1 per cent saponin belonged to this type. More dilute saponin solutions gave foams of the third type in which P increased with ϵ to a maximum and then decreased to an abrupt end when the foam started breaking around the internal cylinder. In 0.05 per cent saponin foam, P reached the value of 140 dynes/cm^2.

The bubble size of their foams [see equations (32) and (33)] was not determined by Rozenfel'd and Savitskaya, but they observed that the "expansion factor" $\rho/[\rho]$ (see section 62) for a given frother varied with concentration as did P. Thus for 0.3, 0.6, 1 and 2 per cent sodium butylnaphthalenesulfonate, $\rho/[\rho]$ was 55, 75, 50, and 50 while the greatest P was 50, 70, 60, and 60 dynes/cm^2, respectively.

Section 71. A magnitude incorrectly termed "modulus of elasticity" in the original publication has been measured on a chain of soap bubbles[20]. The apparatus used to produce such chains is illustrated in Fig. 35. The soap solution from resorvoir A drops on the capillary opening K closing this for a time. Air coming from D blows these drops into bubbles and pushes the bubbles into enlarged nozzle C. When the frequency of drop formation and the rate of air flow are judiciously chosen, every succeeding bubble remains in contact with its predecessor, and a chain of bubbles (a "unidimensional foam") forms. If an iron particle is attached to the bottom of the lowest bubble and pulled downward by a magnet, the chain extends. For example, a 15 cm long chain of three bubbles was extended by 1.35 cm by a force of 74 dynes, and a 31 cm long chain of six bubbles elongated by 11 cm when a force of 133 dynes was applied. If l is the initial length, Δl the elongation, and f the stress, $E = fl/\Delta l$ is the modulus of elasticity. This equation cannot be applied to Dewar's results as the cross section of the specimen (i.e., of the films in the chain) is not known. Dewar substituted force for stress in the above equation.

The 31 cm long chain broke when the force was a little increased above 133 dynes. If the radius of the film common to two bubbles is R, then its perimeter is $2\pi R$ and the capillary force along the perimeter is $2\pi\gamma R$. As γ of a soap solution is near 30, $2\pi\gamma R$ is about 200 R dynes. If this force was overcome by about 133 dynes, R was about 0.66 cm,

which is a possible value. No attempt to account for the observed value of the breaking load could be found in the original paper.

Section 72. From the theory of elasticity, the modulus of elasticity E and the Poisson ratio σ are functions of the modulus of compression

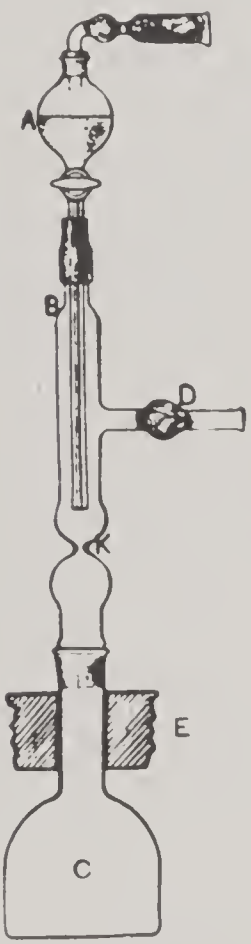


FIGURE 35. Apparatus for producing chains of soap bubbles. Soap solution from A drops on orifice K and is blown to bubbles by air coming through D. The bubbles expand in C. From *Proc. Roy. Inst. Gt. Brit.*, **22**, 359 (1918).

(bulk modulus) k and the shearing modulus μ, as expressed by the equations $E = \mu(3\lambda + 2\mu)/(\lambda + \mu)$ and $\sigma = \lambda/2(\lambda + \mu)$, λ being $k - \frac{2\mu}{3}$. Quantity k is equal to $-v\frac{dP_e}{dv}$ of section 65. Introducing its value from equation (26) and the value of μ from equation (33), the expressions

$$E = \frac{2P_c(3P_e + 2P_c)}{5P_e + 4P_c} \tag{34}$$

and

$$\sigma = \frac{5P_e + 2P_c}{10P_e + 8P_c} \tag{35}$$

are obtained[16]. As P_c usually is much smaller than P_e, σ should be almost equal to 0.5, i.e., the volume of foam restrained on two opposite planes only should not change during contraction or expansion. The value of E should not differ much from $\frac{6}{5} P_c$. These conclusions apparently have not been checked.

Section 73. Resistance of foam to deformations of rather indefinite kind was repeatedly used as criterion of the "quality" of foam. Thus the "stability" of whey-protein foam was judged[26] from the rate of descent of a glass tube stuck in a vertical position in a whipped foam. It was found, for example, that this descent was retarded by adding calcium salts to the whey. Similarly, the "strength" of a malt liquor foam was estimated by placing a glass rod in vertical position on the bottom of a cylindrical vessel filled with froth, releasing the rod, and noting the time which elapses before the rod tilts so far as to touch the wall[27]. This time was longer in the foam of 0.6 per cent malt solution than in either more concentrated or more dilute solutions. Schmalfuss[28] described many mechanical properties of foams produced by beating aqueous solutions of sugar and a frother (lecithin, agar, etc.). The majority of these properties, e.g., the ability of forming sharp edges or tall standing cylinders, cannot readily be correlated with fundamental mechanical quantities.

The wide range of mechanical responses of foam films is illustrated by the well-known difference between the rigidities of soap films and saponin films. When a soap bubble is blown at the orifice of a glass tube, it can be made greater or smaller by blowing in or sucking out air, and these alternate changes can be repeated any number of times without affecting the smoothness of the bubble wall. On the contrary, when air is withdrawn from a saponin bubble, the bubble surface becomes wrinkled.

Section 74. When the rate of shear between two concentric cylinders (i.e., in an apparatus differing from that used by Deryagin and Obukhov [section 69] mainly by the greater length of the internal cylinder) increases, foam seems to get liquid[29]. If foam is treated as a liquid, we may speak of its *viscosity* (see also Chapter 12, section 13). The apparent viscosity, as given by a concentric cylinder viscometer,

decreases when the applied stress increases at least for two foams, namely that of a potassium stearate solution[30] and of an insecticide containing an "inorganic salt" and "an organic colloid."[31]

This insecticide was frothed in an egg whisk. When the volume percentage of air (φ) in the froth was 51.5, 69 and 73 per cent, the ratio η / η_0 was 7.1, 20.3, and 23.2, respectively; η stands for viscosity of the froth and η_0 for viscosity of the liquid, both at high rates of shear at which η and η_0 become approximately independent of the velocity gradient. The results obtained can be summarized by an equation of the type suggested by Hatschek[32], i.e.,

$$\frac{\eta_0}{\eta} = 1 - (1.23\varphi)^{1/3} \tag{36}$$

The equation makes no reference to any surface property, such as surface tension or capillary pressure, and cannot be reconciled with the view that the apparent viscosity of foam depends on the resistance of its films to deformation (see section 69). It is not known what takes place in a foam subject to continuous shearing.

In another instrument foam is pressed through an annular space between an immobile glass tube and a coaxial brass rod suspended on a spring. The "friction" between the foam and the rod causes extension of the spring and can be calculated from it[33]. Foam was made by bubbling air through 6 per cent solution of a hydrolyzed protein stabilized with iron salts. The tractive force exerted by it on the brass rod increased with the foam velocity (which was varied by applying different pressures) and the relative volume of air in the foam. The last mentioned observation may mean that the force was greater for thinner films which suffered greater deformation at a constant velocity than thicker films did. No explanation is offered in the original paper.

The surface finish of the brass rod was not varied in the above experiments. It is interesting to note that rough surfaces are said[34] to be better wetted by foam than smooth surfaces.

Section 75. Extreme mechanical deformation leads to *rupture*. When the foam film has a definite surface tension γ, the linear stress required to break the film is equal to 2γ (because the film has two sides) (see also section 71). The relation between the γ of a film and of the parent solution is considered in section 98.

A fundamental property of surface tension is that, in the equilibrium state, it is independent of the degree of extension or contraction of the surface (if this variation of the surface area has no effect on the composition of the surface). Many foam films have a tension which, like that of a rubber sheet, depends on the degree of surface deformation. Saponin films belong to this class (see section 73). When such a film is ruptured, the breaking stress is not equal to 2γ. Films formed on concentrated solutions or sols of saponins, proteins, etc. or remaining after protracted drainage of foams of similar solutions consist of saponin, protein, etc., that do not differ from these materials which never passed through the stage of foam. In other words, the breaking stress of a, say, protein film is determined by the material of the film itself and is, as a rule, practically independent of the surface tension of solution from which the film originated. Thus it need not be considered in a book on foam.

Rigid films, such as those of dry proteins, can exist for an indefinite time and perish because of observable reasons (e.g., mechanical impact or bacterial decomposition). On the contrary, films which do not become rigid collapse without any discernible cause. This is the reason why persistence of foam has to be treated statistically (see section 28), as the theory of probability is "*le supplément le plus heureux à l'ignorance*" (Laplace).

That many, perhaps the majority of, foam films are destroyed by external causes seems to follow most directly from the fact (see section 18) that films kept in closed vessels often persist for longer time than those in open vessels. The destructive agents such as air currents, dust carrying a foam-breaker, vapors of an anti-froth substance, etc., are less likely to reach a film spanned in an air-tight container.

The probability theory of the rupture of foam films originated with Plateau[35]. He noticed that films broke later the smaller their area and made the following comment: "If, as a rule, persistence diminishes when the film dimensions increase, this seems to me to be due simply to the fact that the greater the film, the greater the chance that one or another point of it succumbs to a rupturing agent. However, another influence has to be born in mind. It acts in the opposite direction. The thinning caused by the suction exerted by the small concave surfaces present all along the perimeter of a film is, of necessity, slower the greater the film area at a constant perimeter and, at a constant area, the smaller the perimeter; from this it is readily

deduced that in a circular ring the slowness of thinning increases with diameter." The small concave surfaces referred to in the above passage are called Plateau's borders in this book (see section 15). The increase of slowness of drainage with diameter was expressed mathematically in equation (20), section 57. Unfortunately this expression would not be easy to test since the amount of liquid draining from one film is small and since the thickness of films usually is not uniform enough to allow its optical measurement.

Plateau expected the slower drainage of larger films to be a factor increasing their persistence as compared with that of smaller films. However, Plateau himself showed that drainage is not a direct factor in the longevity of films. Soap films containing glycerol and kept in humid air *increased* in thickness (because of absorption of water vapor) but snapped just as soon as draining films. Correlation seems to exist between film thickness and resilience as defined in section 76, rather than between film thickness and lifetime.

Section 76. *Resilience* of a film may be defined as its ability to restore its original shape after being pierced by a missile. This property was described first by Dupré[36]. Lead granules and cork balls were dropped through films of soap in aqueous glycerol without rupturing the films. This was possible as long as the missile was not too great and fell from a not too great height; cork balls having diameters of 1 to 1.2 cm ruptured the film when they were released 25 cm or more above the film. Rhumbler[37] studied columns, rather than single films, of soap foam. Iron filings fell through these without leaving any visible track of destruction. Dewar[38] repeated Dupré's experiments using liquid air, mercury, lead shot, and drops of water or soap solution and noticed that very thin films were less resilient than thicker ones. No resilience is shown by mixed films of sodium oleate and saponin[39].

The decrease of resilience on aging has recently been investigated more thoroughly[40]. A shower of mercury droplets (rate of flow 0.3 g/sec) fell from the height of 2 cm on films of 0.43 per cent solution of disodium α-tocopheryl phosphate monohydrate. The average persistence of these films (not bombarded by mercury) was about 420 sec and about 35 sec when the radius was 1.0 and 3.5 cm, respectively (see section 18). The mercury shower was turned on when the films were t' sec old and continued until the film burst; the duration of the shower is denoted here by t''. Thus the films were $t' + t''$ sec old in

the moment of rupture. Fig. 36 shows the decline of t'' (ordinate) when t' (the left-hand curve) and $t' + t''$ (the right-hand curve) increase, all for films 1 cm in diameter. Films of 3.5 cm resisted the impact for 4.5 to 5.3 sec if they were 5 sec old at the start of bombardment, and for only 2.1 to 2.5 sec. if t' was 20 sec. Analogous decrease of resilience on aging was observed also for a neutral and an acid sodium laurate solution, a "benzalkonium chloride" solution, and beer.

The importance of the experiments described in this section for the theory of foam is made clear in sections 97 and 102.

While the earlier observers did not notice any difference between the destructive action (on foam) of materials as different as lead

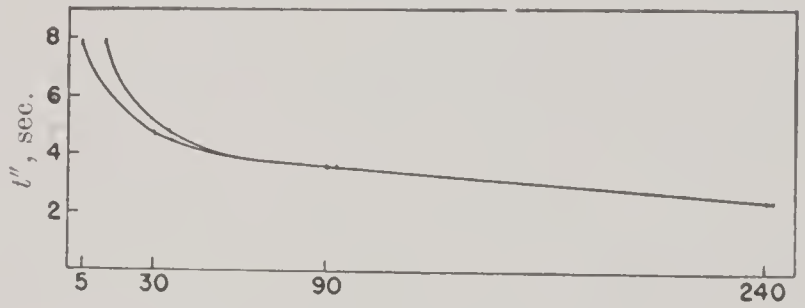


FIGURE 36. Decrease of resilience of foam films on aging. Upper curve: age at rupture ($t' + t''$); lower curve: age at start (t'). Ordinate: duration of shower until rupture. From *J. Phys. Chem.*, **56**, 164 (1952).

granules, cork balls, or liquid air, Shkodin[40a] claims that solids wettable by the foam can, and those unwettable cannot break a froth. This conclusion was based on the observation that the foam (produced pneumatically) of molasses was more readily destroyed by a glass stirrer coated with paraffin wax than by the uncoated stirrer.

Some attempts have been made to destroy foams by high-frequency vibrations. For instance, air vibrating 6,000 times per second was capable of breaking froths such as are used in coal flotation[40b] or form during saturation and evaporation of crude sugar solutions[40c].

Section 77. Dupré[41] attempted to calculate the speed with which a hole made in a film expands or the fim contracts from the hole. Consider the moment at which the hole is S cm^2 big. As the film has two surfaces, the total area of the film decreased before this moment by

$2S$, and its surface energy by $2\gamma S$; γ is surface tension. The energy thus released must, according to Dupré, be completely converted into the kinetic energy of the liquid. The mass of the liquid initially present in S cm^2 of the film was $S\delta\rho$ g, δ being the film thickness and ρ the density. Hence the kinetic energy is $\frac{1}{2}S\delta\rho u^2$, u being the velocity we wish to calculate. From $2\gamma S = \frac{1}{2}S\delta\rho u^2$, the equation

$$u = \left(\frac{4\gamma}{\delta\rho}\right)^{1/2} \tag{37}$$

follows. The velocity of contraction thus appears to be independent of the extent of contraction. Setting $\gamma = 36$ g/sec^2, $\delta = 10^{-4}$ cm, and $\rho = 1$ g/cm^3, we obtain $u = 1{,}200$ cm/sec or about 25 miles per hour. However, equation (37) can give only the upper limit of u as a part of the surface energy released must be used up to overcome the friction in the liquid and another is converted into kinetic energy of the air which must be disturbed by the collapse of the film.

Section 78. Foam films can be broken by nonmechanical means also. Many observations of this kind are reported in Chapter 15. Only a few are mentioned in this section.

Foam rising above a boiling liquid may be destroyed by placing a hot wire above the liquid surface[42]. The temperature and the position of the wire are such that the bubbles burst at least 1 cm from the wire. This prevents deposition of the solute on the wire and possibility of scorching the deposit formed. In all probability the films rupture because of evaporation of the solvent, caused by the radiant heat of the wire. The phenomenon has not been studied quantitatively. The method was tried out on "alkaline pumping liquors." The foam of boiling salt solutions can be broken by forcing it through a spark gap[43]. It is unknown whether the sparks act through the heat evolved or by another mechanism.

Chaminade[44] destroyed froth by radioactive irradiation. A box was filled with aged froth of a solution of sodium lauryl sulfate (5 per cent) and ammonium sulfate (6 per cent) in aqueous glycerol containing also sodium alginate and lauryl alcohol. A polonium preparation emitting 55,000 α-particles/sec was placed 0.5 cm above the froth, one cm^3 of which consisted of 1,600 bubbles. The froth started breaking at such a rate that 0.1 ± 0.05 bubble was destroyed by one α-particle. The rate of collapse slowly decreased, and collapse finally

ceased when there was a depression in the foam underneath the polonium source and the walls of the depression were 3.8 cm distant from the source. This distance (3.8 cm) is the length of the trajectory of α-particles of Po in air. When the irradiation was too strong (over 10,000 α-particles per sec and cm^2), the liquid from the ruptured bubbles enhanced the stability of the lower layers, and the efficiency of bombardment was small.

Ader[45] continued Chaminade's work and found that bubbles ruptured first in 3 cm distance from the polonium preparation. At this distance the ionising action of the α-particles has a maximum. When a flat slab of froth was deposited on a glass plate near a polonium emitter, the slab was gradually cut in two, and the cut was approximately 3 cm from the emitter.

References

1. Henry, W. C., and Barbour, A. D., *Ind. Eng. Chem.*, **25**, 1054 (1933).
2. Barmore, M. A., *Colo. Agr. Expt. Sta., Tech. Bull.*, **9** (1934).
3. Bailey, M. I., *Ind. Eng. Chem.*, **27**, 973 (1935).
4. Williams, H. E., *Ind. Eng. Chem.*, **18**, 361 (1926).
5. Gray, P. P., and Stone, I., *Wallerstein Labs. Comm.*, **3**, 159 (1940).
6. Clark, N. O., "A Study of Mechanically Produced Foam for Combating Petrol Fires," London, Dept. Sci. Ind. Research, 1947.
7. Constable, F. H., and Mergen, S., *Rev. faculté sci., Univ. Istanbul*, **A 12**, 190 (1947); *Chem. Abs.*, **41**, 6454 (1947).
8. Siehr, A., *Kolloid-Z.*, **77**, 27 (1936).
9. Hay, R. L., Reid M., and Pearce, J. A., *Can. J. Research*, **25F**, 160 (1947).
9a. Brenner M. W., McCully, R. E., and Laufer, S., *Am. Brewer*, **84** (2) 39, 49 (1951).
10. King, E. G., *J. Phys. Chem.*, **48**, 141 (1944).
11. Ross, S., *J. Phys. Chem.*, **50**, 391 (1946).
12. Kuzin, S. A., *Tsvetnye Metal.*, **1936**, 45; quoted by Mit'kevich, G. M., *J. Applied Chem. (U.S.S.R.)*, **21**, 816 (1948).
13. Aleinikov (Alejnikoff), N. A., *Tsvetnye Metal.*, **6**, 1546 (1931); *Kolloid-Beihefte*, **36**, 82 (1932).
14. Aleinikov, N. A., *J. Applied Chem. (U.S.S.R.)*, **22**, 812 (1949).
15. Siehr, A., *Kolloid-Z.*, **85**, 70 (1938).
16. Deryagin (Derjaguin), B., *Kolloid-Z.*, **64**, 1 (1933).
17. Plateau, J., *Mém. acad. roy. sci. Belgique*, **33** (1861). 5th ser., p. 29.
18. Dupré, A., *Ann. chim. phys.* [4] **7**, 406 (1866), especially pp. 411–417.
19. Dewar, J., *Proc. Roy. Inst. Gt. Brit.*, **22**, 179 (1917).
20. Dewar, J.,, *Proc. Roy. Inst. Gt. Brit.*, **22**, 359 (1918).
21. Clark, N. O., and Blackman, M., *Trans. Faraday Soc.*, **44**, 1 (1948).
22. Mit'kevich, G. P., *J. Applied Chem. (U.S.S.R.)*, **21**, 816 (1948).
23. Schiebl, K., *Chem.-Ztg.*, **55**, 169 (1931).
24. Bikerman, J. J., *J. Colloid Sci.*, **5**, 349 (1950).

25. Deryagin (Derjaguin), B., and Obukhov (Obuchow), E., *Kolloid-Z.*, **68,** 243 (1934); *J. Phys. Chem.* (*U.S.S.R.*), **7,** 297 (1936).
25a. Rozenfel'd, L. M., and Savitskaya, E. M., *Kolloid. Zhur.*, **13,** 454 (1951).
26. Peter, P. N., and Bell, R. W., *Ind. Eng. Chem.*, **22,** 1124 (1930).
27. Mit'kevich, G. P., *J. Applied Chem.* (*U.S.S.R.*), **22,** 846 (1949).
28. Schmalfuss, H., *Kolloid-Z.*, **116,** 161 (1950).
29. Blackman, M., *Trans. Faraday Soc.*, **34,** 8 (1948).
30. Ostwald, Wo., and Malss, H., *Kolloid-Z.*, **63,** 305 (1933).
31. Sibree, J. O., *Trans. Faraday Soc.*, **30,** 325 (1934).
32. Hatschek, E., *Kolloid-Z.*, **8,** 34 (1911).
33. Grove, C. S., *et al.*, *Ind. Eng. Chem.*, **43,** 1120 (1951).
34. Kodak-Pathé, French Patent 942,087; *Chem. Abs.*, **44,** 10391 (1950).
35. Plateau, J., *Mém. acad. roy. sci. Belgique*, **37** (1869). 9th ser., p. 7.
36. Dupré, A., "Théorie mécanique de la chaleur," p. 352, Paris, Gauthier-Villars, 1869.
37. Rhumbler, L., *Ergeb. Physiol.*, **14,** 526 (1914).
38. Dewar, J., *Proc. Roy. Inst. Gt. Brit.*, **24,** 197 (1925).
39. Shkodin, A. M., and Tikhomirova, G. P., *Kolloid. Zhur.*, **13,** 134 (1951).
40. Bikerman, J. J., *J. Phys. Chem.*, **56,** 164 (1952).
40a. Shkodin, A. M., *Kolloid. Zhur.*, **14,** 213 (1952).
40b. Shiou-Chuan Sun, *Mining Eng.*, **3,** 865 (1951).
40c. Parlow, R., *Zucker*, **3,** 468 (1950); *Chem. Abs.*, **45,** 911 (1951).
41. Dupré, A., "Théorie mécanique de la chaleur," p. 350, Paris, Gauthier-Villars, 1869.
42. Gastrock, E. A., and Reid, J. D., *Ind. Eng. Chem., Anal. Ed.*, **10,** 440 (1938).
43. Schnurmann, R., *Ind. Eng. Chem., Anal. Ed.*, **11,** 287 (1939).
44. Chaminade, R., *Compt. rend.*, **228,** 480 (1949).
45. Ader, *J. phys. radium*, **11,** 198 (1950).

6. OPTICAL PROPERTIES OF FOAMS

Section 79. The striking colors of soap films are caused by the *interference* of light reflected from the two surfaces of the lamellae. A mathematical expression for this interference can be deduced using Fig. 37. In it δ is the thickness of the film. The beam of light coming from A is partly reflected at the phase boundary giving rise to beam BC and partly refracted (beam BO). The refracted beam is reflected from the opposite phase boundary at O and finally is refracted into the gas space at D (beam DE). There is a phase difference between the two resulting beams, one of which reached the line CD, normal to BC and to DE, coming from B in air, while the other travelled from B to O and D in the film. From Fig. 37, BC $= 2\delta \tan \beta \cdot \sin \alpha$ and (BO + OD) is $2\delta/\cos \beta$. As the wavelengths in air (λ_0) are n times those in the lamella, if n is the refractive index of the latter, the *optical* path of the beam BOD is $2n\delta/\cos \beta$. The difference between the two optical paths is, then, $\Delta = (2n\delta/\cos \beta) - 2\delta \tan \beta \cdot \sin \alpha$ or

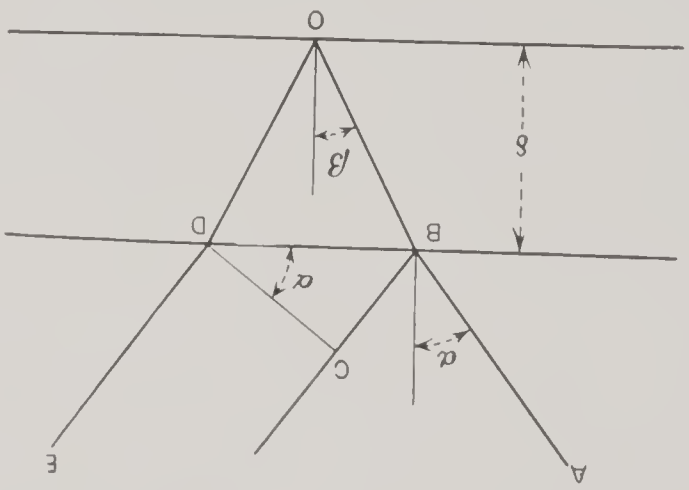


FIGURE 37. Reflection of light from foam lamellae.

$$\Delta = 2n\delta \cos \beta \tag{38}$$

since $\sin \alpha \cdot \sin \beta = n \cdot \sin^2 \beta$. As function of the angle of incidence α,

$$\Delta = 2\delta(n^2 - \sin^2 \alpha)^{1/2} \tag{39}$$

The difference expressed in wavelengths is

$$\frac{\Delta}{\lambda_0} = \frac{2n\delta \cos \beta}{\lambda_0} \tag{40}$$

As light advances by $\lambda_0/2$ when reflected from an (optically) denser medium, 0.5 has to be added to the right-hand side of equation (40) to obtain the difference between the numbers of wavelengths in the two beams. Therefore, when $\frac{\Delta}{\lambda_0}$ is equal to $^1/_2$, $^3/_2$, $\cdots$, this difference is one, two, $\cdots$ whole wavelengths, the two beams are in phase, and the reflected light is at its brightest. When $\frac{\Delta}{\lambda_0}$ is 0, 1, 2, $\cdots$, then the difference is $\frac{\lambda_0}{2}, \frac{3\lambda_0}{2}, \frac{5\lambda_0}{2}, \cdots$, the two beams cancel each other, and no light is reflected.

Clearly, examination of a film in monochromatic light allows determination of its thickness. Thus (see equation (39)) there are maxima of reflection when δ is equal to $\frac{\lambda_0}{4(n^2 - \sin^2 \alpha)^{1/2}}, \frac{3\lambda_0}{4(n^2 - \sin^2 \alpha)^{1/2}}$ etc. Hence, if the angles α corresponding to two or more succeeding maxima of brilliancy have been determined, δ can be calculated. This is possible, however, only as long as δ is either smaller than λ_0 or not much greater than λ_0; when δ/λ_0 is large, the difference between two successive α is too small.

When the incident light is white and the reflected beam is viewed in a spectroscope, dark bands are visible. If their number is m between the wavelengths λ' and λ'', λ' being greater than λ'' and both being measured in air, then

$$\delta = \frac{m\lambda'\lambda''}{2n \cos \beta(\lambda' - \lambda'')}. \tag{41}$$

This equation is readily deduced starting from (40). There is darkness when $2n\delta \cos\beta$ is equal to a whole number of wavelengths. Suppose this number is k for λ', i.e.,

$$2n\delta \cos \beta = k\lambda' \tag{42}$$

At some smaller wavelength, say λ''', $2n\delta \cos\beta$ will be equal to $(k + 1)\lambda'''$, and so on, until the wavelength λ'' is reached. As there are m bands between λ' and λ'' (including one of these), $2n\delta \cos \beta = (k + m)\lambda''$. From this and equation (42) it follows that $k\lambda' = (k + m)\lambda''$, i.e., $k = m\lambda''/(\lambda' - \lambda'')$. Setting this expression for k into (42) yields (41).

Section 80. Equations of section 79 are not sufficient to determine the *color* of a thin film. If (see equation (40)) $2n\delta \cos \beta$ is equal to the wavelength of, for example, sodium light ($\lambda_0 = 589$ mμ), then this part of the spectrum will be extinguished or weakened, and the film will have the complementary tint, i.e., appear blue or violet. A more precise description of this color cannot be given as long as purely physical (as opposed to physiological) viewpoint is taken. Prediction is even more difficult if more than one wavelength is extinguished. Thus, $2n\delta \cos \beta$ may be equal to two wavelengths of a red ($\lambda_0 = 680$ mμ) and three wavelengths of a blue ($\lambda_0 = 453$ mμ), and both these parts of the spectrum will be weakened in the reflected light.

An approximate equation for the intensity I of the reflected light is

$$\frac{I}{I_0} = K \sin^2 \frac{2\pi n\delta \cos \beta}{\lambda_0}. \tag{43}$$

I_0 is the intensity of incident light and K is a constant showing what fraction of this intensity is reflected under the most favorable conditions, i.e., when $\sin(2\pi n\delta \cos \beta/\lambda_0) = 1$. If it is assumed that K is independent of wavelength (which need not be always true) and n is also (this assumption is always inexact), then I/I_0 is a simple function of $\delta \cos \beta$ and λ_0 and can be calculated for any number of different wavelengths and any value of $\delta \cos \beta$. If in addition it is known what is the physiological color of light whose intensity I is known as function of λ_0, then the quality of the color can be determined.

Rayleigh[1] carried out such a calculation and obtained results summarized in Table 8. Corresponding graphs complying with the modern international standards have been traced by Kubota[2], but only for thin layers between air and glass and thin layers of air between two glass plates. In Table 8 each color is expressed as sum of three standard colors, namely, orange red ($\lambda_0 = 630.2$ mμ), green ($\lambda_0 = 528.1$ mμ), and blue ($\lambda_0 = 456.9$ mμ). To obtain color which appeared as white to J. C. Maxwell's wife, the intensities of these three rays had to be 3.973, 6.520, and 6.460 arbitrary units; these units are used in Table 8. To obtain pure spectral colors it was necessary to mix chiefly two of the three standards, the intensity of the third being about 5 per cent of the total intensity or less. This means that the colors in the table are purer (spectrally) the smaller the contribution of a third component. The first column of the table contains the values of $2n\delta \cos \beta$ in μ ($= 10^{-4}$ cm). If the light falls normally on the film (i.e.,

$\cos \beta = 1$) and $n = 1.4$ (as for many soap solutions), then the values of the first column must be divided by 2.8 to obtain the film thickness in 10^{-4} cm. The other columns show the intensities of the three standard colors which, combined, would reproduce the color of the

TABLE 8. COMPOSITION OF LIGHT REFLECTED FROM FILMS OF THICKNESS δ

$2n\delta \cos\beta$ in 10^{-4} cm	Intensity (Arbitrary Units) $\lambda_0 = 630.2$	$\lambda_0 = 528.1$	$\lambda_0 = 456.9$in	$2n\delta \cos\beta$ 10^{-4} cm.	Intensity (Arbitrary Units) $\lambda_0 = 630.2$	$\lambda_0 = 528.1$	$\lambda_0 = 456.9$
(white	3.973	6.520	6.460)				
0.2725	3.82	6.46	5.87	1.408	2.69	4.72	1.42
0.3519	3.75	5.07	2.79	1.435	3.06	4.30	1.95
0.4060	3.01	3.20	0.82	1.462	3.33	3.78	2.68
0.4342	2.51	2.23	0.27	1.516	3.51	2.75	4.15
0.4569	2.04	1.49	0.18	1.570	3.20	2.01	5.03
0.4751	1.67	1.01	0.27	1.624	2.53	1.77	4.93
0.4997	1.20	0.53	0.69	1.678	1.75	2.11	3.97
0.5281	0.75	0.26	1.63	1.732	1.09	2.82	2.74
0.5449	0.49	0.26	2.25	1.787	0.76	3.56	1.85
0.5831	0.13	0.67	3.81	1.814	0.74	3.87	1.71
0.6302	0.09	1.82	5.44	1.841	0.83	4.12	1.75
0.7120	0.99	4.44	5.87	1.868	1.00	4.26	1.99
0.7923	2.59	5.95	3.37	1.895	1.26	4.32	2.41
0.8392	3.29	5.77	1.71	1.922	1.55	4.27	2.91
0.8933	3.78	4.68	0.59	1.976	1.86	4.13	3.41
0.9204	3.81	4.04	0.58	2.003	2.45	3.69	4.17
0.9475	3.74	3.17	0.93	2.057	2.83	3.16	4.48
0.9745	3.50	2.40	1.59	2.111	2.93	2.76	4.02
1.029	2.68	1.26	3.42	2.166	2.72	2.56	3.24
1.083	1.67	0.93	5.08	2.220	2.35	2.62	2.45
1.137	0.79	1.48	5.71	2.274	1.89	2.85	2.28
1.191	0.29	2.68	5.02	2.328	1.52	3.47	2.98
1.245	0.35	3.96	3.43	2.382	1.32	3.17	2.52
1.299	0.91	4.91	1.86	2.436	1.34	3.65	3.69
1.326	1.33	5.13	1.31	2.490	1.53	3.73	4.04
1.353	1.79	5.17	1.03	2.545	1.83	3.67	3.84

light reflected by the film. For example, the intensities for $2n\delta \cos \beta = 0.2725\ \mu$ are very similar to those found for white; hence the film appears almost white in reflected light. If the ratios of the numbers in the 2nd, 3rd, and 4th columns are equal, then the shades of the light reflected are identical although the intensities may be different. Thus the ratios at a value of $2n\delta \cos \beta$ somewhere between 0.4060 and 0.4342μ will be almost equal to those at $2n\delta \cos \beta = 0.9204\ \mu$, but the overall intensity is greater for the thicker film.

Section 81. The colors represented in Table 8 belong to the first five orders. When the film thickness increases starting from nothing, the tints more or less repeat themselves. Every succession of colors ending in red is an order. The names given to the tints slightly vary according to the observer. Reinold and Rücker[3] compiled the following list. The numbers mean the values of $n\delta$ (not $2n\delta$) corresponding to the center of the band having the color designated left of the number.

First Order	Second Order		Third Order	
Black	Purple	0.305 μ	Purple	0.559 μ
White	Blue	0.353 μ	Blue	0.603 μ
Yellow	Green	0.409 μ	Green	0.656 μ
Red	Yellow	0.454 μ	Yellow	0.710 μ
	Orange	0.491 μ	Red	0.765 μ
	Red	0.522 μ	Bluish red	0.815 μ

Fourth Order		Fifth Order		Sixth Order	
Green	0.893 μ	Green	1.188 μ	Green	1.479 μ
Yellow-green	0.964 μ	Red	1.335 μ	Red	1.627 μ
Red	1.052 μ				

Seventh Order		Eighth Order
Green	1.787 μ	Green starts at 2.004 μ
Red	1.936 μ	Red starts at 2.115 μ

These values determined experimentally on soap films may be compared with, and supplemented by, the data of Table 8. Thus the white of the first order has $2n\delta$ of about 0.27 μ (i.e., $n\delta = 0.135$ μ) as the composition of the light reflected by such films is nearly that of white (it is a yellowish white since there is a slight deficiency of blue). The tint is identical with that of orange red of $\lambda_0 = 630.2$ mμ when the intensities of green (528.1) and blue (456.9) in Table 8 are in the same proportion as in white while the relative intensity of orange red is greater than in white. In the first order this state is reached at $2n\delta = 0.49$ μ approximately, and the color corresponding to $2n\delta = 0.50$ μ may be termed red.

The change of color on changing the film thickness is particularly sudden when the color moves from one end of the spectrum (red) to the other (purple), i.e., between the first and second and between the second and the third orders. The $n\delta$ corresponding to the first "sensitive violet" (or purple), as these colors are known, is usually given as 0.280 μ.

The colors nearest to pure spectral colors are a bluish violet of the second order ($2n\delta = 0.6302\ \mu$), a yellow of the 2nd order ($2n\delta = 0.9204\ \mu$), and a blue of the third order ($2n\delta = 1.191\ \mu$). The best greens of the 3rd and the 4th order ($2n\delta = 1.326\ \mu$ and $2n\delta = 1.841\ \mu$, respectively), although they contain considerable amount of white, are very brilliant. At greater thicknesses, when $2n\delta$ is greater than, say, 2 μ, the hues are little sensitive to thickness δ. The deterioration of colors occurring on increase of δ can be shown by the values of the successive minima of the intensities listed in Table 8. For $\lambda_0 = 630.2$ mμ they are 0.09, 0.29, 0.74, and 1.32, for $\lambda_0 = 528.1$ mμ 0.26, 0.93, 1.77, and 2.56, and for $\lambda_0 = 456.9$ mμ 0.18, 0.58, 1.03, 1.71, and 2.52. When δ increases, spectral purity of the reflected light tends to decrease.

Section 82. Table 8 embraces only films for which $2n\delta \cos \beta$ is 0.2725 μ or greater. Fig. 38 illustrates a method of judging the hues of thinner films[4]. Its ordinate shows the luminosity of rays whose wavelength is plotted along the abscissa. The upper curve is for white light; it has a maximum in green because the sensitivity of human eye to green is greater than to any other color, and when the physical intensity of all colors is equal, green appears the most intense. To obtain physiological intensities, i.e., luminosities, the intensities calculated from equation (43) must be multiplied with the sensitivty of the eye to the wavelength concerned. The results of this multiplication are shown along the ordinate of Fig. 38 for several very thin films. The abscissa represents frequency, here the number of vibrations in 10^{-12} sec. The figures marked at the curves mean $n\delta$ of the film in units equal to 6×10^{-7} cm; thus the luminosity of a film whose $n\delta$ is 6×10^{-7} cm is shown by curve 1. This luminosity is minute, and the film is black. As long as $n\delta$ is very small, $\sin^2 (2\pi n\delta/\lambda_0)$ is approximately equal to $(2\pi n\delta/\lambda_0)^2$, i.e., increases four times when λ_0 decreases to one-half from extreme red to extreme violet. The variation of the sensitivity of the eye with λ_0 is greater. Hence the luminosity curve of very thin films (curve 5) looks like a very depressed sensitivity curve somewhat shifted toward blue, and the film appears grey. At $n\delta = 138 \times 10^{-7}$ cm (i.e., 0.138 μ, curve 23) the film is white, and at $n\delta = 0.234\ \mu$, curve 39, it is yellow. Between curves 46 and 47 ($n\delta = 0.276$ and 0.282 μ, respectively) the colors are "sensitive."

Equation (43) allows calculation of the product $n\delta$. A more complicated optical method yields the values of n and δ separately. It is

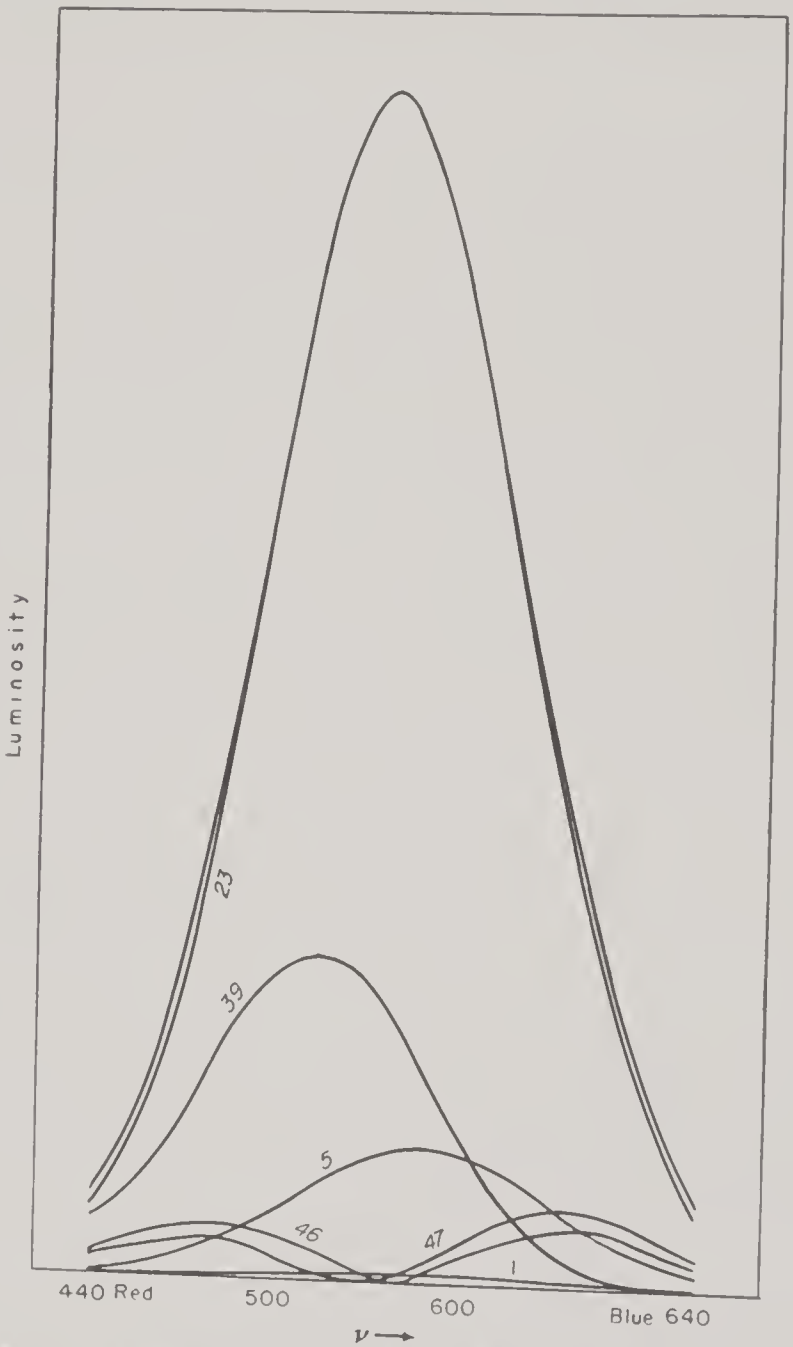


FIGURE 38. Physiological intensity of light reflected by foam films. Abscissa: number of vibrations in 10^{-12} sec. Figures at the curves are $n\delta$ in units of 6×10^{-7} cm. From *Ann. phys.* [9] **16**, 69 (1921).

based on the ellipticity of light reflected by a thin film when the incident beam is plane polarized[5]. The azimut of the restored plane of polarization and the phase difference are measured. The calcula-

tion of n and δ from the results of measurement cannot be indicated here (see ref. 6). This method is particularly useful for foam films thinner than those showing white of the first order. Its application is mentioned in section 91.

Section 83. In sections 79 to 82 the optical properties of single films were reviewed. Of the optical properties of multicellular foams only light transmission seems to have been measured[7]. White light of intensity I_0 traversed a layer, 1 cm thick, of foam and decreased in intensity during the process. A part of this decrease was due to absorption of light in the liquid present in the foam. If the intensity of the emergent light, corrected for this absorption, is I, it is found that $\frac{I_0}{I} = \frac{a}{R} + b$, R being the average radius of the bubble and a and b constants. If it is remembered that the number of bubbles traversed by the beam along the 1 cm stretch is $N = \frac{1}{2R}$, the above relation can be written as

$$\frac{I_0}{I} = 2aN + b \tag{44}$$

Evidently b should be equal to 1, as there is no loss in intensity when $N = 0$, but experiments for three solutions of hydrolyzed keratin gave about -16 as the value of b, while a 5 per cent solution of potassium coconut oil soap really yielded $b = 1$. The theoretical deduction of equation (44) given in the original paper does not appear convincing and is not reproduced here. The ratio I/I_0 was 0.05 for $N = 45$ and 0.02 for $N = 80$ in a foam of 5 per cent hydrolyzed keratin; that is, 80 bubbles reduced the intensity of light to 1/50th of the initial value.

References

1. Rayleigh, J. W. S., *Scientific Papers*, **2**, p. 498, University Press, Cambridge.
2. Kubota, H., *J. Optical Soc. Am.*, **40**, 146 (1950).
3. Reinold, A. W., and Rücker, A. W., *Trans. Roy. Soc. (London)*, **172**, 447 (1881).
4. Wells, P. V. *Ann. phys.* [9] **16**, 69 (1921).
5. Drude, P., *Ann. Physik* [3] **43**, 158 (1891).
6. Vašiček, A., *J. Optical Soc. Am.*, **37**, 145 (1947).
7. Clark, N. O., and Blackman, M., *Trans. Faraday Soc.*, **44**, 7 (1948).

7. ELECTRICAL PROPERTIES OF FOAMS

Section 84. Not much is known concerning electrical properties of foam. For example, no measurement could be found of the dielectric constant of a froth. However, electrical conductance has been determined for both single films and multicellular foams.

For the measurements on single films, direct current and needle electrodes were used. The disadvantage of direct current (polarization of the electrodes) is well known. Unfortunately the usual method is difficult to apply because of the variable thickness of the film (see below). The procedure worked out by Reinold and Rücker was as follows[1, 2, 3]. A large foam film is produced. Two gold needles are made to pierce it, current of known intensity is sent through the needles, and the potential difference φ between them is determined. Then the needles are immersed to depth δ_0, at the same mutual distance, in the solution (of conductivity κ_0) from which the foam was made, the same current is sent through them, and the potential difference φ_0 is measured. If the film thickness determined optically (see Chapter 6) is δ, then the specific conductivity κ of the film is

$$\kappa = \frac{\delta_0 \varphi_0}{\delta \varphi} \kappa_0 \tag{45}$$

It is clear that equation (45) can be applied only if δ has a definite value, i.e., the film has a constant thickness between the electrodes and over a considerable area around them. This is a condition not easy to realize. A measure of success was achieved only after a special arrangement for humidifying the atmosphere around the film has been built. The films were vertical, and the direction of the current was from the upper to the lower needle. It was ascertained that the ratio $\delta_0\varphi_0/\delta\varphi$ was not affected by the carbon dioxide of the atmosphere or the moisture of the air (although uptake or loss of water altered thickness δ), and did not vary with the intensity of the current. Within the (large) limits of error this ratio was independent of temperature between 19° and 26°. When a film which had thinned to, say, first sensitive purple (section 81) was flooded and then allowed to thin again, the ratio assumed its previous value.

The experimental results described in the 1893 paper are somewhat different from those reported earlier and alone are reviewed here. It was found that the ratio $\delta_0\varphi_0/\delta\varphi$ was never smaller than one and depended on δ and the nature of the solution. For the thicknesses 97, 296, and 641 mμ this ratio was 4.47, 1.98, and 1.66, respectively, when the solution consisted of 1 part sodium oleate and 60 parts water. For a foam of sodium oleate 1 part, potassium nitrate 1.8 part, and water 60 parts, the ratio varied irregularly between 1.0 and 1.27; and it was not distinguishable from one for a solution made up of 3 volumes of the just mentioned liquid and 2 volumes of glycerol.

To account for these observations Reinold and Rücker[3] introduced, ten years before Smoluchowski, the notion of surface conductance. They pictured the film as consisting of two surface layers, each x cm thick, and interior liquid whose thickness, then, was $\delta - 2x$. If the specific conductivity of the surface layer is κ_s, that of the interior liquid κ_1 and that of the liquid in bulk κ_0, then

$$\frac{\kappa}{\kappa_0} = \frac{2x\kappa_s + (\delta - 2x)\kappa_1}{\delta\kappa_0} \qquad \text{or} \qquad \frac{\kappa}{\kappa_0} = \frac{\kappa_1}{\kappa_0} + \frac{2x(\kappa_s - \kappa_1)}{\delta\kappa_0} \tag{46}$$

If equation (46) were correct, the ratio κ/κ_0 (or $\delta_0\varphi_0/\delta\varphi$) would be linear function of $1/\delta$ and the intercept of the straight line with the axis at $(1/\delta) = 0$ would show the ratio of the conductivities κ_1 and κ_0. The three values mentioned in the previous paragraph are not in agreement with equation (46), but still seemed to Reinold and Rücker to indicate that κ_1 was not equal to κ_0. The second term of the right-hand side of equation (46) contains two unknowns (x and κ_s), if the difference between κ_1 and κ_0 is neglected, and thus cannot be used to calculate them.

However, unpublished calculations show that the above experimental data can be accounted for by the modern theory of surface conductance (see, e.g., ref. 6, p. 387), if it is assumed that the two faces of a soap lamella are lined with unimolecular films of fatty acid anions with the corresponding cations forming two diffuse double layers in the liquid body of the lamella.

Section 85. Hagenbach[4] conducted similar experiments on films of 1 part sodium oleate + 40 parts water + 4 parts glycerol. Taking the conductivity of a film 780 mμ thick for the standard (κ_0) he found

the ratio κ/κ_0 to be 1.79 for $\delta = 300$ mμ, 1.71 for $\delta = 272$ mμ, 2.58 for $\delta = 164$ mμ, 2.71 for $\delta = 140$ mμ, and 2.57 for $\delta = 121$ mμ. In spite of the considerable spread of the values it is clear that the ratios, as a rule, are greater the smaller δ. A quantitative evaluation, such as by means of equation (46), evidently is impossible.

Different results were obtained with a different set-up[4]. A horizontal soap film was produced in a dish. The lid of the dish contained two platinum needles which pierced the film when the lid was put on. Then the dish, including the lid, was rotated in the horizontal plane. Because of centrifugal force the liquid gradually thinned starting from the middle. In monochromatic light, bright and dark rings moved toward the periphery of the film. When the needles were in the middle of, for example, a bright ring, the electric current strength between them was determined. At constant applied voltage it was proportional to the film thickness between 200 and 1200 mμ. The δ was determined optically.

Rickenbacher[5] using the second method of Hagenbach observed proportionality between current strength and δ when the latter varied from 100 to 500 mμ. An increase in conductivity was, however, noticed at the lower limit of this range.

Section 86. Surface conductance of a liquid usually is associated with electric double layer near the surface, that is, with electrokinetic effects (see, e.g., ref. 6). One of the four major electrokinetic phenomena is electroösmosis, i.e., movement of liquid in constant electric field. Such a movement was observed by Reinold and Rücker[7]. Downward electric current accelerated the drainage of a vertical film of a potassium soap solution, while upward current prevented thinning and, when sufficiently strong, caused even oozing of droplets at the wire from which the film was hanging. Thus, the aqueous solution was positive and the surface layers were negative. A property common to nearly all electrokinetic effects is their depression by relatively large amounts of electrolytes. The reduction of surface conductance caused by 1.8 part potassium nitrate in 60 parts water (see section 84) thus is in agreement with the view classifying the observations of Reinold and Rücker among electrokinetic effects. Unfortunately the authors made no reference to electrokinetics and no measurements followed their qualitative statements. This renders

comparison of electroösmosis and surface conductance in foam films impossible until new experimental data have been procured.

Section 87. The electric conductance of *multicellular foam* of a synthetic detergent was shown to be proportional to the amount of

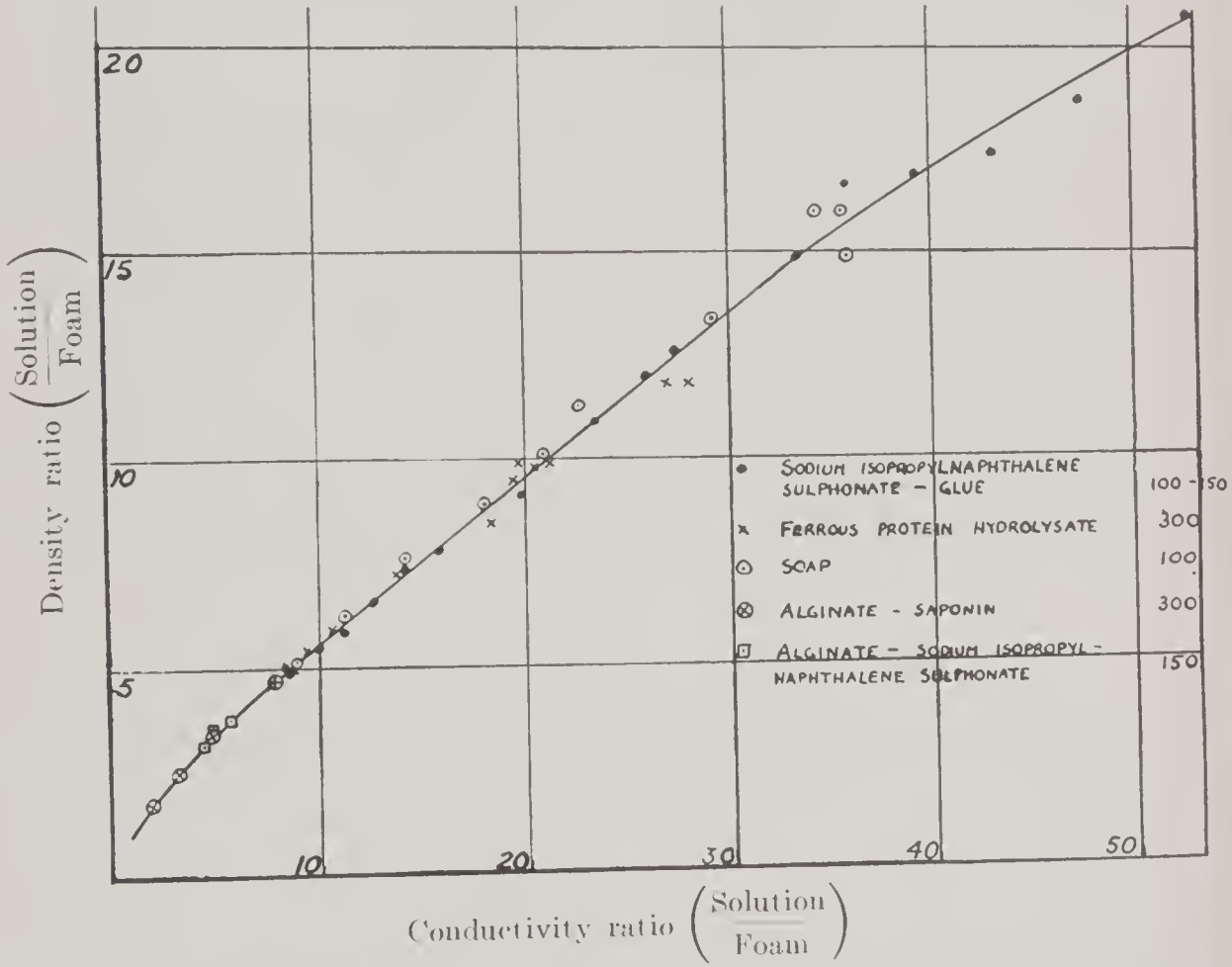


FIGURE 39. Electrical conductivity and density of foams. From *Trans. Faraday Soc.*, **44**, 13 (1948).

liquid in the froth[8]. A more definite regularity was noticed by Clark[9]. Fig. 39 combines his results for five aqueous solutions whose conductivities ranged from 2×10^{-4} (sodium alginate + saponin) to 5×10^{-3} ohm^{-1} cm^{-1} (ferrous protein hydrolyzate). The ratio of the densities of liquid and foam, i.e., $\rho/|\rho|$ (see section 62) is plotted along the ordinate, while the abscissa represents the ratio of the electric conductances liquid: foam. It is seen that one curve suffices for all the solutions tested; that is, by "diluting" a liquid with air its conductance is reduced in a ratio independent of the specific conductivity

of the liquid. The ratio of the conductances $\kappa_0/[\kappa]$, $[\kappa]$ being the conductance of foam, is greater (e.g., 50) than the ratio of the densities $\rho/[\rho]$ (e.g., 20) for the same system. As no explanation of this fact is attempted in the original publication, the following qualitative discussion may be welcome.

Clearly, conductance is lowered not only because there is less liquid but also because this liquid is distributed in an unfavorable manner. Imagine foam as aggregation of cubic bubbles (see Fig. 40a), and let the current flow in the direction of the arrow. The films normal to the arrow (and the plane of the paper) do not participate in the transport of electricity. Thus two out of six sides of every cube make no contribution to conductance. A better approximation is

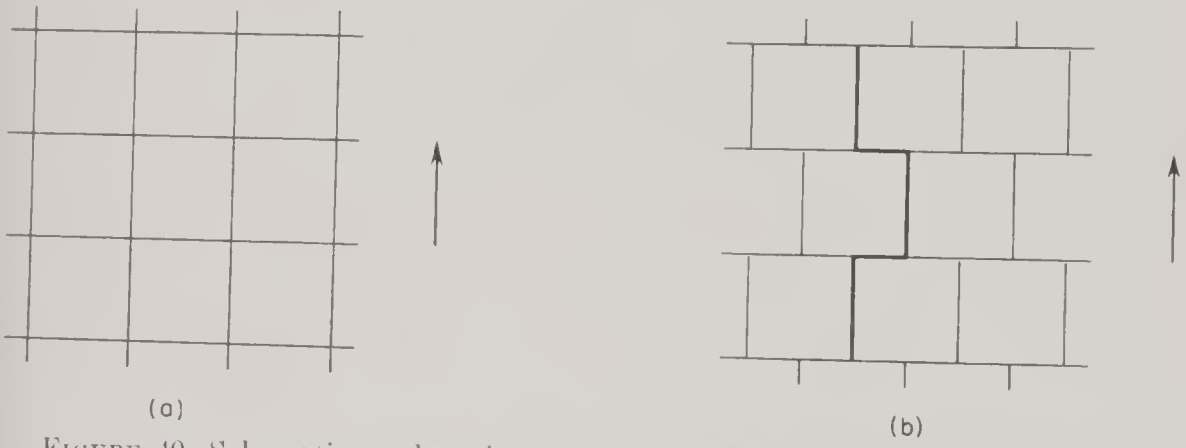


FIGURE 40. Schematic explanation of the results of Figure 39. See in text.

achieved by likening foam to the system of Fig. 40b in which (see section 15) not more than three films come together in a liquid vein. It is seen that the films normal to the arrow not only fail to increase the width of the path open to electricity but actually increase the length of this path, as exemplified by the thick line in Fig. 40b. If this second effect is about as great as that illustrated in Fig. 40a, the experimental ratio of $\kappa_0/[\kappa]$ to $\rho/[\rho]$ which is approximately 2 to 2.5 is readily obtained. If the *disposition* of the films is responsible for the smallness of $[\kappa]$, this ratio may be expected to be independent of bubble size. This was the case for the foams of Fig. 39.

Section 88. Two soap bubbles often can be slightly pressed against each other without coalescence. In the presence of an electrified body (such as rubbed stick of sealing wax) they immediately form one

bubble[10]. Apparently this interesting effect has never been studied in quantitative manner.

References

1. Reinold, A. W., and Rücker, A. W., *Trans. Roy. Soc. (London)*, **172,** 447 (1881).
2. Reinold, A. W., and Rücker, A. W., *Trans. Roy. Soc. (London)*, **174,** 645 (1883).
3. Reinold, A. W., and Rücker, A. W., *Trans. Roy. Soc. (London)*, **A184,** 505 (1893).
4. Hagenbach, A., *Arch. sci. phys. et nat.*, **35,** 329 (1913).
5. Rickenbacher, W., *Kolloidchem. Beihefte*, **8,** 139 (1916).
6. Bikerman, J. J., "Surface Chemistry for Industrial Research", New York, Academic Press, 1948.
7. Reinold, A. W., and Rücker, A. W., *Phil. Mag.* [5] **19,** 94 (1885).
8. Miles, G. D., Shedlovsky, L., and Ross, J., *J. Phys. Chem.*, **49,** 93 (1945).
9. Clark, N. O., *Trans. Faraday Soc.*, **44,** 13 (1948).
10. Boys, C. V., "Soap Bubbles and the Forces which Mould Them", page 131, London, Society for Promoting Christian Knowledge, 1890.

8. RADIUS OF MOLECULAR ACTION. BLACK SPOTS

Section 89. Extremely thin foam films have been of great importance to the molecular theory. Laplace's explanation of surface tension is based on the idea of a sphere of molecular action. Molecules whose spheres of action lie wholly within the liquid are neither attracted by, nor repelled from the surface, while on molecules whose distance from the surface is less than the radius of this sphere a resultant force acts directed to the interior of the liquid. When the liquid is present as a film thinner than the diameter of the sphere of action, no molecule has its sphere filled with liquid, there is less difference between the molecules near to and further from the surface, and surface tension of such films should be less than that of liquid in bulk and also should decrease as the film thickness decreases. Thus, if surface tension γ of films of gradually diminishing thicknesses is determined and that thickness δ_m is found at which γ starts to decrease, this δ_m is the diameter of the sphere of molecular action.

Plateau[1] was the first to attempt measurement of δ_m. He blew soap bubbles at one end of a vertical U-tube partly filled with water. The meniscus in the open half of the tube was higher than in the half closed by the soap bubble since in the interior of a bubble of radius R the pressure is by $4\gamma/R$ higher than the atmospheric (see section 64). If, then, the bubble was allowed to drain without altering its shape (i.e., R), change in the relative position of the menisci would signify a change in γ. No such change was visible even when the films were as thin as Plateau could produce. His thinnest film was 0.114 μ ($= 1.14 \times 10^{-5}$ cm), optically determined (section 79) so that the radius of molecular action must be less than 0.057 μ.

Similar experiments have been performed by G. L. Van der Mensbrugghe (1866, 1867). Reinold and Rücker[2] blew two soap bubbles at the opposite ends of a glass tube. The bubbles had equal dimensions, hence also equal capillary pressures ($4\gamma/R$), and there was no transport of air between them. Then one of the bubbles was allowed to drain, while the liquid in the other bubble was replenished from time to time. It was expected that, as soon as the wall thickness

of the first bubble descends below δ_m, a difference in γ and capillary pressures between the two bubbles would be established and air transport would be noticed. This did not happen even in films as thin as 0.012 μ ($= 1.2 \times 10^{-6}$ cm) (optically determined). The sensitivity of the instrument was claimed to be such that 0.5 per cent change in γ would be detected. The radius of the sphere of molecular action then would be less than 0.006 μ.

Drude[3] used soap films as magnifying glass. He viewed an object through a soap bubble with a telescope. In thinning, the bubble showed patches of different colors, i.e., also of different thicknesses. When the object was viewed first through, say, a thick and then a thin part, the magnification remained unaltered. This proves that the curvature of the bubble was constant independently of the wall thickness. Thus, γ also must have been constant because there can be only one value of the capillary pressure $4\gamma/R$ inside a bubble. The thinnest spot for which the constancy of γ could thus be demonstrated was 0.017 μ thick.

Johonnot[4] lifted a cylindrical film by a glass ring from the surface of a 2 per cent sodium oleate solution and measured the pull on the ring when the film was so thick as to show no color, when its thickness became 0.012 μ, and when it was 0.006 μ (both determined optically). The change in the pull, i.e., also in surface tension, was not more than 1 to 2 per cent.

Section 90. Black patches are often seen in foam films of sufficient stability (soaps, sodium α-tocopheryl phosphate, and so on). A film must look black or nearly black when it is very thin (see section 83). But "black spots" are not only very thin; they also qualitatively differ from thicker lamellae. All the observations reported in this section have been made on various soap films as black films of other compositions were not made objects of quantitative study.

Black patches almost always are contiguous to fields of a much greater thickness, and the boundary is so sharp that no transition is visible in a microscope. Around a usual black spot there must be a step, a phenomenon unexpected in a liquid. Black patches appear to offer particular resistance to liquid movement. When electric current is sent through a soap film, the shape, size, and color of all the colored fields in it vary, but the black spots may remain unaffected[5]. When a black area is produced in the center of a horizontal film by rotating

this in its plane (see section 85) and the centrifuging is stopped, the liquid accumulated along the periphery of the film starts moving back toward the center, and the currents can be followed by color changes, but the liquid does not penetrate into the black field[6].

It was long believed that black films differ from colored films also in that they have one definite thickness (for a given system) while colored films can have any thickness [provided that their $n\delta$ is greater than, say 0.14 μ (see section 83)]. Now it is known that several black films are possible (see section 93) but it is still true that black spots which spontaneously form in soap films usually have thicknesses more or less characteristic of the solution used.

Section 91. These thicknesses were determined either by optical or by electric measurements. If light passes through many black films arranged one behind the other in a tube, the total difference in the optical path is the sum of the differences caused by single films and can be estimated from the color of the reflected light[7]. The total optical thickness divided by the number of the films gives the average value of $n\delta$ (n is refractive index, δ thickness). The difference in the optical paths between two geometrically equal paths, one in air and the other in air and a series of black films, can also be determined by the displacement of fringes in a Michelson interferometer[8]. If Δ is this displacement and N the number of films, $\delta = \lambda_0\Delta/2N(n - 1)$. λ_0 is the wavelength in air. Alternatively, the thickness can be estimated from the ellipticity of light reflected by one film (see section 82). The electrical determination of δ is based on the assumption that the conductance of a thin film (thickness δ) is to the conductance of a thick film (thickness δ_1) as $\delta:\delta_1$, i.e., that $\kappa = \kappa_0$ [see section 84, equation (45)].

Optical measurements of the thickness of the most common black film gave 12 mμ for 2 per cent solution of sodium oleate[8] and 16 to 17 mμ for a sodium oleate solution in aqueous glycerol[3]. The very extensive experiments of Reinold and Rücker[9] are not in agreement with these results. They yielded the following values for the thickness of black films of 1 part sodium oleate in x parts water:

x =	30	40	60	80
δ =	22	22	28	29 mμ

A solution of sodium oleate in 40 volumes water and 27 volumes

glycerol had $\delta = 25$ mμ. These values are greater than the comparable values found by the other investigators.

Reinold and Rücker made a remarkable observation which, apparently, has not been checked by any later scientist. When the solution, besides 2.5 per cent sodium oleate, contained 0.5, 1.0, or 3 per cent potassium nitrate, the thickness of the black film was lowered from 22 to 14.5, 13.5, and 12.4 mμ, respectively. In the presence of 3 per cent potassium nitrate, δ did not markedly depend on the soap concentration. As the existence of surface conductance in soap films makes the existence of electric double layers in them very probable (see section 86), it is tempting to correlate the decrease of δ caused by an electrolyte to similar phenomena attributed to the interference of electric double layers. Some aged hydroxide sols form, on standing, parallel horizontal layers of thin plates separated from the next layers by intermicellar liquid or more dilute sol. The mutual distance of these layers is nearly constant in a given sol and can be determined interferometrically as it is about as great as the wavelength of visible light. When an electrolyte is added to such a system, the distance between the layers decreases[10]. Presumably this decrease is due to contraction of the double layer (see, e.g., ref. 11). The effect of potassium nitrate on δ may have the same cause.

On this view, the thickness of black films is determined by the contrary actions of drainage and the mutual repulsion of two electric double layers. At small δ this repulsion steeply increases when δ decreases. When on thinning of the lamellae the repulsion becomes equal to the forces causing drainage, drainage stops, and δ remains constant. Foreign electrolytes diminish the repulsion, and the equilibrium between it and the suction tending to remove liquid is attained at a smaller δ. This (unpublished) theory semiquantitatively accounts for the experimental data.

Section 92. There is no agreement between δ determined from electric conductivity (section 84) by different observers. The thickness of the usual black film of 2.5 per cent sodium oleate solution in water or aqueous glycerol was stated as 13 to 14 mμ[6], 37 to 54 mμ[12], and 148 to 154 mμ[9]. Addition of 3 per cent potassium nitrate lowered δ to 11 mμ[9] or 12 to 15 mμ[12]. The great ratio of "electrical δ" to "optical δ" in the experiments by Reinold and Rücker and the depression of this ratio by potassium nitrate well accord with the theory of

section 86. In the presence of 3 per cent potassium nitrate the "electrical δ" (11 mμ) was found even smaller than the "optical δ" (12 mμ) but this difference probably does not exceed the experimental error. The "electrical δ" was 13 mμ when 2 per cent potassium nitrate was added, 24 mμ for 1 per cent potassium nitrate, and 26.5 mμ for 0.5 per cent potassium nitrate[9].

Section 93. The existence of more than one black film was known in the nineteenth century, but Perrin[13] discovered a whole series of black films. He used solutions of soap and a dye or of rosin soap, but 5 per cent aqueous potassium oleate solutions without any addition serve just as well[14]. The films are observed in a microscope provided with a vertical illuminator so that the observer's eye receives reflected light only. After aging, these films exhibit fields each having a definite thickness, and these thicknesses are multiples of the least thickness. Thus the films are *stratified*, they consist of elementary leaflets, all identical, placed one on top of the other in numbers which vary from one to another field. Presumably they are similar to fresh "built-up" multilayers (see ref. 11, p. 254) and different from ordinary foam films. In the latter, there is liquid between the two surface layers. The least amount of liquid present presumably is determined by the mutual repulsion of the two double layers (see section 91). Slightly greater liquid layers may be unstable, but considerably thicker liquid layers should be possible whatever their thickness. On the contrary, stratified lamellae contain only a very small amount of liquid, and this liquid is not concentrated in the middle layer of the lamella but seems rather to be spread in thin layers between the successive layers of soap (or fatty acid, see section 106).

Whatever the exact structure of Perrin's lamallae, it is certain that the thickness of various fields is a multiple of a fundamental length. This has been shown by two procedures. The simpler requires only a microscope with vertical illuminator. When a horizontal soap film, 0.1 to 0.2 cm in diameter, is allowed to thin, it is seen that the film thickness diminishes in steps. For example, in blue light of λ_0/n = 0.354 μ (λ_0/n is the wavelength in the soap solution), 17 steps were counted when the lamella thinned from a black to maximum luminosity and again 17 when it thinned further to the next minimum of brightness. There was no further decrease in thickness, showing that

the last black corresponded to the thinnest possible film. Hence, the maximum must have belonged to $\delta = 0.0885\ \mu$ (equal to a quarter of the wavelength used) and the earlier minimum to $\delta = 0.177\ \mu$ (see section 79). As the numbers of steps were equal along the two equal intervals of δ, it is likely that all steps were equal, each being $88.5/17 = 5.2$ mμ[13]. This is, approximately, the length of two soap molecules.

In the more elaborate procedure the thickness of every lamella is determined. Either the intensity I of the light reflected by the lamella is compared with that of light which passed through two nicols making angle α with each other, or the color of the film is duplicated in a quartz wedge. In the first method the intensity of light is proportional to $\cos^2 \alpha$; from the measured α the ratio I/I_0 (I_0 is the intensity of incident light) is calculated, and from it δ is found by means of equation (43)[13, 14]. In the second method[15], δ is to thickness δ_q of the wedge having the right color as $2n$ is to $n_0 - n_e$, n being the refractive index of the film, and n_0 and n_e these indices for ordinary and extraordinary rays of quartz. As $n_0 - n_e = 0.009$ and $2n = 2.8$, δ_q is 311 δ and can readily be measured. The first method yielded 4.1 mμ for the thickness of the unit leaflet of films of 5 per cent potassium oleate in water or aqueous glycerol.

Presumably Perrin's lamellae thin by evaporation rather than by drainage. When water evaporates, the remaining soap forms mesomorphous systems[16]. In common with other mesomorphous structures, stratified soap films have peculiar mechanical properties. Water droplets (produced, for example, by breathing on the lamella) easily move along the lamellae which support their weight without sagging (although the droplets may have diameters of 100,000 δ) but do not offer any considerable resistance to the movement in the plane of the film. However, the wandering droplets never cross the boundary between two different fields, e.g., 10 mμ and 5 mμ thick[13] (see section 90).

Section 94. Since the black field as a rule has a sharp boundary against the next, much thicker field, the velocity of spreading of the black is not difficult to measure. However, the few results published seem to be mutually contradictory[17]. An example which appears to show the relative importance of gravitation and Plateau's borders as causes of drainage (see section 56) may be mentioned explicitly[18]. The advance of black in a *hanging* bubble was slower the farther the

black progressed; this was attributed to suction by Plateau's borders surrounding the top of the bubble. In a *sessile* bubble the advance of black was more rapid the greater the black field because suction by Plateau's border assisted gravitation. The area invaded by black within three days was equal for both bubbles, but this presumably was a coincidence.

References

1. Plateau, J., *Mém. acad. roy. sci. Belgique*, **33** (1861), 5th ser.
2. Reinold, A. W., and Rücker, A. W., *Trans. Roy. Soc. (London)*, **177**, 627 (1886).
3. Drude, P., *Ann. Physik* [3], **43**, 158 (1891).
4. Johonnot, E. S., *Phil. Mag.* [6], **11**, 746 (1906).
5. Reinold, A. W., and Rücker, A. W., *Phil. Mag.* [5], **19**, 94 (1885).
6. Hagenbach, A., *Arch. sci. phys. et nat.*, **35**, 329 (1913).
7. Reinold, A. W., and Rücker, A. W., *Trans. Roy. Soc. (London)*, **174**, 645 (1883).
8. Johonnot, E. S., *Phil. Mag.* [5], **47**, 501 (1899).
9. Reinold, A. W., and Rücker, A. W., *Trans. Roy. Soc. (London)*, **184**, 505 (1893).
10. Zocher, H., *Z. anorg. allgem. Chem.*, **147**, 91 (1925).
11. Bikerman, J. J., "Surface Chemistry for Industrial Research," p. 402, New York, Academic Press, 1948.
12. Rickenbacher, W., *Kolloidchem. Beihefte*, **8**, 139 (1916).
13. Perrin, J., *Ann. phys.* [9], **10**, 180 (1918).
14. Wells, P. V., *Ann. phys.* [9], **16**, 69 (1921).
15. Marcelin, R., see Marcelin, A., *J. chim. phys.*, **28**, 605 (1931).
16. Friedel, G., *Ann. phys.* [9], **18**, 273 (1922).
17. Dewar, J., *Proc. Roy. Inst. Gt. Brit.*, **21**, 786 (1916).
18. Dewar, J., *Proc. Roy. Inst. Gt. Brit.*, **22**, 359 (1918).

9. THE THEORY OF FOAMS

Section 95. Foam forms when bubbles in a liquid do not coalesce either with each other or the continuous gas phase, although they are surrounded by only a thin wall. Whatever cause exists or whatever device is invented to keep bubbles as separate units, it will produce foam. No special study is needed to reject any theory attributing foam formation to a particular chemical property or structure, such as "hydrogen bonds" or "polar-unpolar molecules." In Chapter 11 foams are discussed in which coalescence of bubbles is prevented by solid particles. When there are two phases only, the following general statements may be made.

Mutual approach of two bubbles or approach of a bubble to the continuous gas phase necessitates pushing liquid aside. This pushing is slowed down by viscosity. Hence, if viscosity is great enough, coalescence does not occur or occurs very slowly. However the dispersion thus obtained would be a gas-in-liquid emulsion rather than a foam (see section 1), since viscosity retards thinning of liquid interstices also when they are relatively thick. As far as viscosity is concerned, real foam is produced when the viscosity η of thick liquid layers is small, thus enabling the bubble quickly to cover the major part of the distance to the neighboring gas phase, but η of thin layers is great, wherefore crossing the last part of this distance takes a long time.

Phenomena of this kind are common when bubbles rise in a hot liquid toward cool air. The surface layer of the liquid is colder than the bulk and, therefore, has higher viscosity. The bubbles rapidly rise almost to the surface but do not easily break the thin layer separating them from the continuous gas phase. Often this thin layer solidifies when the bubble lifts it and thus facilitates its cooling. The foams of furnace slags, mentioned in section 49, form by this mechanism. The viscosity of a liquid surface can be greater than that of the bulk also when the temperature is constant throughout the system. If, for example, the liquid (e.g., molten metal) contains impurities (e.g., metal oxides) which are lighter than the main constituent of the liquid, the impurities concentrate at the surface because of gravita-

tion. If the viscosity of the impurities is greater than that of the bulk at the same temperature, relatively stable foam may result.

Section 96. Enhanced viscosity of thin liquid layers adjacent to gas phase, also in the absence of the obvious phenomena mentioned in section 95, was postulated by Plateau[1] and named *viscosité propre des couches superficielles* or *surface viscosity* for short. Plateau believed to have demonstrated its existence by experiment. He suspended a metal needle either in the surface of a liquid or just under the surface and showed that the resistance to rotation of the needle (in the horizontal plane) was greater in the first case. This behavior was observed not only for strongly foaming solutions, such as of a soap, but also for water. Marangoni[2] detected the fallacy of Plateau's method. When a needle rotates in the surface of a liquid, it compresses the impurities in the front of it and leaves clean ("swept") liquid surface behind. As surface tension of clean liquid is greater than that of contaminated liquid, the needle is pulled with a greater force backward than forward, and the resulting force (which opposes rotation) simulates enhanced viscosity. Nevertheless a method analogous to that of Plateau's was used as late as 1939[3].

Marangoni's objection does not apply to the procedure in which a disc or a ring is rotated, rather than a needle (see, e.g., refs. 4 and 5). Instead of comparing the resistances to rotating a fully submerged and a partly submerged ring (or disc), the resistance of a pure (water) and a contaminated (e.g., soap solution) surface can be compared, the ring being immersed to the same depth in both instances. Another method uses the time required for contaminated surface to invade clean surface as a measure of surface viscosity[6]. Both methods were applied chiefly to surfaces covered with unimolecular layers. Neither of them affords absolute values for surface viscosity, and it is not known how reliable the relative values are. Still, although exact measurement of surface viscosity has not succeeded yet, the existence of this property in many systems cannot be doubted.

The "normal" (Newtonian) viscosity, however large, can only retard coalescence but cannot prevent it. Many solutions possess "abnormal" viscosities of which the simplest type causes the following behavior: as long as the stress applied remains below a minimum ("yield stress"), no flow takes place, i.e., the material appears solid; but when the stress is greater, the material flows like a liquid.

except that not the whole stress appears active but only the excess of it above the yield stress. The idea of yield stress usually is believed to be fairly recent. However, it was familiar to Gibbs[7] who wrote: "It seems probable, however, that this process (drainage of foam) is often totally arrested by a certain gelatinous consistency of the mass in question, in virtue of which, although practically fluid in its behavior with reference to ordinary stresses, it may have the properties of a solid with respect to such very small stresses as those which are caused by gravity in the interior of a very thin film . . ." The existence of yield stresses in foam films has been pointed out also several times since[4, 8].

The high viscosity or plasticity of foam films presumably is the main cause of the great persistence of protein, saponin, and similar foams. After the bulk of the solvent has evaporated or drained away, the remaining lamellae are solid or almost solid and do not burst for a very long time (see section 75). For other foams, although surface viscosity very probably is a factor in their stability, it certainly is not the only factor. In every investigation comparing foaminess or rate of drainage with surface viscosity of long-chain compounds, considerable discrepancies were found. Thus the rate of drainage during the first minute of foam life was almost identical for "olive textile soap" and "white toilet soap," both in 0.1 per cent solution, although the former liquid had no surface viscosity exceeding that of water while the latter had a very viscous surface[9]. Surface viscosity of sodium laurate solutions was indistinguishable from that of water although these solutions give rise to persistent foams[10]. Trapeznikov[11] compared the lifetime of single bubbles under various monolayers (see section 19) with the surface viscosity of the latter. Monolayers of cetyl alcohol were 10 to 100 times as viscous as those of oleic acid but the persistence of air bubbles under oleic acid was 3 to 4 times as great as under cetyl alcohol. Surface viscosities of ethyl palmitate and cetyl alcohol were very close to each other, yet the bubbles under cetyl alcohol were 5 times as persistent as under the palmitate. When, by compressing a monolayer of cetyl alcohol, its surface viscosity was raised in the ratio 15:1, the bubble lifetime was lowered from 3.2 to 2.1 sec. It is believed that, when the monolayer is brittle, bubbles may escape through the fissures in the film; in this case obviously no relation between surface viscosity and persistence can be expected. The escape through fissures was postulated by Trapeznikov to account for the greater spread of persistences under a stearic acid

monolayer on water than on 0.01N hydrochloric acid. The former layer (which usually contains soaps of multivalent metals) is brittler than the latter (see also section 41).

Section 97. There are two main forces which tend to destroy foam bubbles, namely, surface tension and gravitation. An idea of the relative importance of these forces may be gained by comparing the variations in the surface energy and the energy of gravitation occurring when an isolated bubble is converted into a drop situated at the lowest point of the original bubble. If the surface area of the drop is neglected in comparison with that of the bubble and the wall thickness δ is small compared with the bubble radius R, then the decrease in surface is $8\pi R^2$ and the decrease in surface energy (ΔU_s) is $8\pi R^2\gamma$. The volume of liquid in the bubble being $4\pi R^2\delta$ and its weight $4\pi R^2\delta\rho g$ (ρ is density difference between liquid and gas, and g is acceleration due to gravity), the decrease in the gravitational energy (ΔU_g) is $4\pi R^3\delta\rho g$, since the center of gravity is lowered by R. Hence,

$$\frac{\Delta U_s}{\Delta U_g} = \frac{2\gamma}{R\delta\rho g} \tag{47}$$

Taking $\gamma = 30$ g/sec^2, $R = 1$ cm, $\delta = 10^{-4}$ cm, $\rho = 1$ g/cm^3, and $g = 981$ cm/sec^2, $\Delta U_s/\Delta U_g$ becomes about 600. Thus in an average foam, surface forces are much more destructive than gravitation.

This brings us to the second component of Plateau's theory of foam, which now may be formulated as follows. Foam is destroyed by surface tension but the destruction is retarded by surface viscosity; hence the persistence of a foam increases with the ratio of surface viscosity η_s to surface tension γ. This theory is not in accord with observations. The surface tension values of the solutions mentioned in section 96 are so close that the disagreement between surface viscosity and stability implies disagreement between stability and η_s/γ also. For example, the γ values of the two soaps investigated by Preston and Richardson were almost identical.

The most striking proof of the insufficiency of Plateau's theory is afforded by the experiments described in section 76. Self-healing of a foam film pierced by lead shot or mercury droplets cannot be accounted for by surface tension, surface viscosity, or a combination of both. Surface tension tends to contract the surface rather than to

spread it over damaged area, and viscosity can only retard a movement but cannot reverse its direction. Dry protein foams, which are stable because of their surface viscosity or plasticity (see section 96) do not "heal" when pierced by a projectile.

Section 98. The phenomenon now believed to be the main cause of stability of many foams was pointed out by Marangoni[2] and Rayleigh[13].

If the composition of the surface layer is different from that of the bulk solution, its surface tension is smaller than that of the latter; this was known, for example, to Dupré[12]. If the surface layer is damaged, the underlying solution is exposed. Its greater surface tension pulls the "edges of the wound" together thus causing complete healing of the surface. This effect is easily demonstrated by dusting some ignited talc on the surface of ordinary (not exceptionally clean) water and directing an air blast on the dusted area. The air pushes aside the superficial layer and the talc particles floating in it. When the blast is stopped, the particles are seen to invade the noncontaminated patch. This patch has a cleaner surface, hence a higher surface tension; therefore it contracts.

Marangoni's "law" was formulated by him as follows (ref. 2, p. 260; translation is by Rayleigh[13]): "The surface of a liquid, covered by a pellicle, possesses two superficial tensions; the first which is the weaker and in constant action, is due to the pellicle; the second is in the latent state, and comes into operation only when the pellicle is ruptured. Since the latter tension exceeds the former, it follows that any force which tends to rupture the superficial pellicle upon a liquid encounters a resistance which increases with the difference of tensions between the liquid and the pellicle." This difference of tensions Marangoni called *elastic surface force*. Because the term *pellicle* may be given too literal a meaning, Marangoni later[14] used the expression *contaminated surface*.

A slightly different description of the above phenomenon was given by Gibbs[15]. He defined the *elasticity* of a foam film as "the infinitesimal increase of the united tensions of its surface divided by the infinitesimal increase of area in a unit of surface." If E_s is this elasticity and S surface area of the film, then

$$E_s = 2S \frac{d\gamma}{dS} \tag{48}$$

Whenever the surface layer ruptures as the first step of the rupture of a foam lamella, the exposed surface, having greater γ, contracts and thus causes healing of the fissure. This theory readily accounts for the resilience of lamellae (see section 76). When the lamella becomes so thin that the liquid between the surface layers ceases to have the properties (including surface tension) of the liquid in bulk, the Marangoni effect should be less pronounced and the resilience of the lamella should decrease. This expectation was confirmed, since aged (that is, also thinner) lamellae stood up to a mercury shower for a shorter time than thicker (fresher) films.

The elastic surface force of foam films supplies the explanation for the fact that vertical films are not destroyed by gravitation. The top of such a film has to support the weight of the rest; thus, its tension must be greater than that of the lower parts; hence, surface tension of a vertical film must increase from bottom to top, i.e., from a region of small to the region of strong stretching. An experimental confirmation of this conclusion is given by an observation (by Lüdtge) reported by Van der Mensbrugghe[16]. When a horizontal wire rectangle, whose two opposite sides (A and C) are connected by a thread longer than the sides B and D, is wetted by soap solution, a film remains and the thread may assume any shape in this film. If, however, the rectangle with its film is placed vertically, the thread gradually forms a smooth curve convex to the top. Obviously the higher surface tension of the upper part of the film causes contraction of the area above the thread.

Section 99. For Rayleigh's theory to be applicable (or for Marangoni's effect to be operative), the surface tension of fresh surfaces of solutions capable of foaming should be greater than that of aged surfaces. The truth of this conclusion was known long ago (e.g., to Dupré[12]) but its main quantitative confirmation was achieved by Rayleigh[17].

Several methods are available for determining surface tension of very fresh surfaces (see, e.g., refs. 18 and 19). The method of oscillating jets is particularly convenient[20, 21]. Liquid flows from a vessel through a noncircular orifice. The liquid jet issuing from the orifice is seen to pulsate, or, more exactly, its cross section changes from an ellipse elongated, say, from west to east to a circle, then to an ellipse elongated in the north-south direction, to a circle again, and

so on. The reason for these pulsations is that the jet originally has the noncircular cross section of the orifice. The capillary pressure at the ends of the longer axis of the cross section is greater than at the ends of the shorter axis because the curvature is sharper at the former points; this induces movement which overshoots the equilibrium position (circle) and continues as long as viscosity or external circumstances permit.

The fundamental equation governing the period T of pulsations can be derived by the method of dimensions. T depends on surface tension γ (g sec^{-2}), density ρ (g cm^{-3}) and average radius r (cm) of the jet. Viscosity affects the amplitude of pulsations more than it does T and may be neglected. As $\gamma\rho^a r^b T^c$ must be dimensionless, a must be equal to -1, $b = -3$, and $c = 2$. Hence,

$$\gamma = k\rho \frac{r^3}{T^2} \tag{49}$$

k being a constant (pure number). It depends on the shape of the orifice but usually does not much deviate from unity[20]. If the volume rate of flow is v cm^3/sec, v is equal to the product of the volume of a segment of the jet and the number of these segments produced in a second, i.e., $v = \pi r^2\lambda/T$, λ being the length of a segment. If T from this equation is introduced into (49), formula

$$\gamma = \frac{k\rho}{\pi^2 r}\left(\frac{v}{\lambda}\right)^2 \tag{50}$$

results, which is easier to use than (49) when evaluating experimental data. The value of the constant k can be found by applying equation (50) to the jet of a liquid whose γ is known. The age of the surface is calculated from the linear velocity of the jet, which is $v/\pi r^2$. Let λ in equation (50) be the length of the segment whose center is in l cm distance from the orifice. Then the liquid in this segment has spent $\pi r^2 l/v$ sec outside the vessel, and the age of the surface is $\pi r^2 l/v$ sec.

Table 9 lists some results obtained by Rayleigh[17]. In it, 2λ is the double length of segment in the liquid jet, 0.01 sec old, and h is the capillary rise of the same liquid, both in mm. The method of capillary rise deals with aged surfaces. If the surface tensions of fresh and aged surfaces were identical, the product $2\lambda^2 h$ would be constant since λ^2 is inversely and h directly proportional to γ. It is seen that $2\lambda^2 h$ is greater for water than for foaming substances. The value of 2λ (i.e.,

also of the γ of fresh surfaces) is almost identical for pure water, sodium oleate solutions, and a horse chestnut infusion (i.e., solution of crude saponin), while h (and consequently the steady surface tension) of the solutions is considerably smaller than that of water.

When the liquid in the jet moves farther from the orifice, its age increases. Hence, λ of a segment far from the orifice is sometimes greater than λ near the orifice, and from the variation of λ along the jet the variation of γ in time can be calculated. Fig. 41 from Burcik[10] displays the results of such a calculation for sodium dodecyl sulfate solutions. In the instance of sodium oleate the decrease of γ on aging may be due in part to the chemical reaction with the carbon dioxide of the air, but the rate represented in Fig. 41 is more likely to be determined by the rate of diffusion of the solute to the surface.

Table 9. Surface Tension of 0.01 Second Old and of Aged Surfaces

Liquid	2λ mm	h mm
Water	40.0	31.5
1:40 sodium oleate	45.5	11.0
1:80 sodium oleate	44.0	11.0
1:400 sodium oleate	39.0	11.0
1:4,000 sodium oleate	39.0	23.0
Water	39.2	30.5
Infusion of horse chestnut	39.5	20.7

Section 100. Marangoni's theory accounts for the inability of pure liquids and saturated solutions to foam (see section 32). In these liquids the chemical difference between the surface and the bulk is nonexistent or too small to produce a considerable "elastic surface force."

As foam persistence is zero or nearly zero at both ends of the foaminess-concentration curve, there must be at least one maximum of the persistence at some intermediate concentration. Prediction of this concentration from theoretical considerations has been attempted repeatedly. Thus Quincke[22] believed foam to be "more persistent the more the tension of the free surface is reduced by a layer of another liquid (soap water, protein) which covers the free, i.e., adjacent to air, surface." In quantitative language, if γ_0 is surface tension of pure solvent (or of the very fresh surface of the solution; section 99) and γ is surface tension of the aged solution, then foaminess should be maximum when $\gamma_0 - \gamma$ is maximum.

According to another hypothesis, "the optimum of foam formation

occurs when the boundary layer has the greatest heterogeneity, i.e., when the molecules of the solvent and the dissolved frother are present in the boundary layer in equal numbers[23]." In systems for which the Gibbs adsorption equation is valid, the bulk concentration correspond-

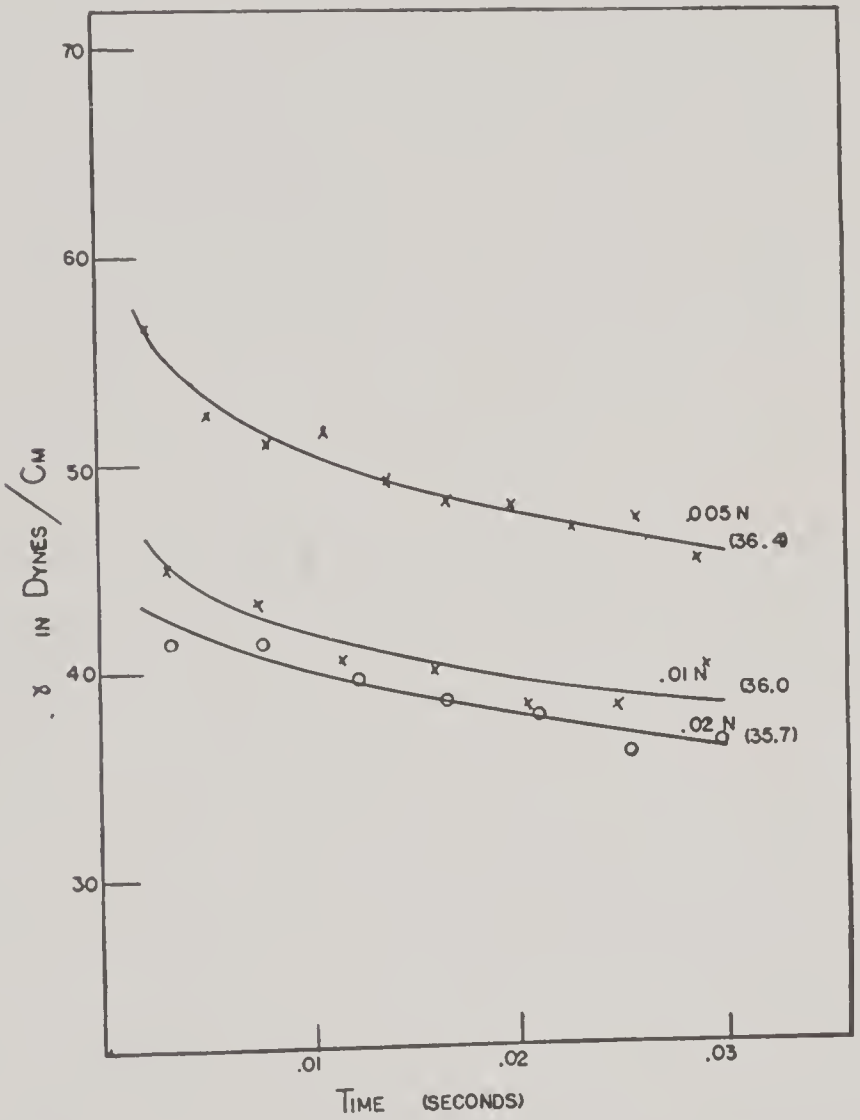


FIGURE 41. Decrease of surface tension on aging. Sodium dodecyl sulfate solutions. Temperature 20.0°C. Figures in parentheses are equilibrium surface tensions. From *J. Colloid Sci.*, **5**, 421 (1950).

ing to the 50:50 composition of the surface layer can be calculated if a particular structure of this layer (e.g., its unimolecularity) is assumed.

Experiments do not confirm Quincke's hypothesis. The difference $\gamma_0 - \gamma$ increases when the concentration of, for example, a lower alcohol in water increases up to the saturation point, while foam

stability, measured in more than one manner, reaches a maximum and then decreases (see section 34). The agreement between the concentration of maximum persistence and that of the maximum value of $d\gamma/dc$, c being the concentration of the solute, is somewhat better. In the usual approximate form of the Gibbs equation, the adsorbed amount is proportional to $-c\frac{d\gamma}{dc}$. This product often passes through a maximum when c increases because $d\gamma/dc$ usually is small at high concentrations. It would be instructive to find out which of the concentrations listed in Table 4, section 34, better agree with the concentrations of the maximum $-c\frac{d\gamma}{dc}$. For many aqueous solutions the longest time of collapse was observed when the surface tension of the solution was confined within the range 54 — 70 g/sec^2. The physical meaning of this observation is not known[23].

It is possible that the concentration of the greatest foam stability is not determined by the equilibrium surface tensions. Marangoni's theory is based on the assumption that the pure surface, bared by pushing aside the surface contaminations, remains pure long enough to bring together the contaminated areas. If, however, surface tension of the exposed surface is very quickly lowered by diffusion of the surface-active solute from the bulk of the solution, the restoring force is weaker or even absent[24]. As a rule, diffusion will be more rapid (i.e., more of the solute will diffuse in unit time) the higher the concentration. Hence the Marangoni effect is weakened at high concentrations, and foam persistence correspondingly decreases. This depression of the Marangoni effect seems to be demonstrated by the two values for more concentrated sodium oleate solutions in Table 9, section 99. It is seen that at a time when surface tension of a 0.25 per cent solution is practically that of water, surface tension of a 2.5 per cent solution is already 14 per cent less than that of water.

Section 101. As a summary of the views discussed in sections 95–100, the following interpretation of foam stability may be given.

When a very high surface viscosity is present, it alone may cause formation of stable foams. When surface viscosity is not unusually high, foams are stable chiefly because surface tension of the external layers is considerably smaller than that of the bulk liquid underneath. When the bulk liquid is exposed by rupture of the surface

layers, surface tension should not decrease to the equilibrium value too rapidly.

The classification of foaming solutions proposed by Shorter[25] may be mentioned here. He sifted foams in three groups: (1) surface concentration thermodynamically reversible, special superficial viscosity or rigidity absent; (2) surface concentration thermodynamically irreversible, special superficial viscosity or rigidity absent; and (3) surface concentration thermodynamically irreversible, the surface layers specially viscous or rigid. Types (1) and (2) correspond to the Marangoni, and type (3) corresponds to the Plateau part of the present theory. Rebinder[26] considers two types of foam stability only, namely with or without surface viscosity or rigidity.

Section 102. While the development associated with the names of Plateau, Marangoni, Gibbs, and Rayleigh may be said to constitute the main stream of the theory of foam, some ideas not connected with it also deserve being reviewed.

Because of evaporation, foam usually will be colder than the surrounding air. This temperature difference was believed to be a factor in foam stability[16, 27]. Van der Mensbrugghe described the following experiment. A wire triangle, dipped into oil of turpentine, withdrawn from it and kept horizontally in air, carries a film stable for a few seconds only. When the same triangle is partly immersed in the oil of turpentine so that one of its sides is submerged but the opposite corner remains above the surface of the liquid, then the film produced in the triangle lasts much longer (17 min. in Mensbrugghe's conditions). The suggested explanation is that the apex of the triangle, because of evaporation, is cooler than its lower parts. The oil moves upward because the cooler liquid has lower surface tension. Thus the film does not thin and has less tendency to rupture than have thinner films.

However, foams are not always cooler than the ambient air. The energy spent on making foam (e.g., by shaking or by bubbling air through a liquid) for a while remains in the foam and thus tends to raise its temperature. Such a temperature rise was observed in a foam of 0.01 per cent saponin solution[28]. Collapse of foams is said to produce no measurable heat effect[29].

The concentration of the surface layer of a solution, as a rule, is different from that of the bulk although osmotic pressure tends to

equalize the concentration everywhere. It was believed that the equilibrium between the osmotic forces and the molecular forces causing accumulation of a component at the surface might be upset when two surfaces come close together, that the osmotic forces are the stronger ones in thin layers, and that they prevent final thinning of the lamellae[30, 31]. This hypothesis has never been cast in a quantitative form. If the picture of soap films as electrokinetic systems (see sections 86 and 91) is correct, then the two surfaces of such a film do not join because of the mutual repulsion of two electrical double layers. This repulsion thus would take over the function attributed to osmotic pressure. It is not certain that electrical double layers capable of noticeable mechanical effects exist in solutions containing but few ions (e.g., dilute alcohols). Solutions of proteins and synthetic ionic detergents should behave in this respect like soap solutions.

It has been repeatedly proposed to account for the lifetime of a foam by assuming that foam films burst when they thin to a definite "critical" thickness[32, 33, 34]. This assumption certainly is not correct as "black films" consisting of one or two bimolecular leaflets of soap (see section 93) are quite durable while numberless foam films break before they show any interference color. However, in view of Bikerman's experiments reported in section 76, the assumption can be modified and thus made more likely. When films have a thickness below some "critical" value, the Marangoni effect ceases to be operative in them and they are easily ruptured by external agents which would not affect a "wetter" film. In this manner a theoretical correlation between foam persistence and rate of drainage is established. The experimental test of such a correlation[33, 34] should be supplemented by new experiments.

References

1. Plateau, J., *Mém. acad. roy. sci., Belgique*, **37**, (1869). 8th ser., p. 49.
2. Marangoni, C., *Nuovo cimento* [2], **5–6**, 239 (1871).
3. Fourt, L., *J. Phys. Chem.*, **43**, 887 (1939).
4. Trapeznikov, A., *Acta physicochim. U.R.S.S.*, **9**, 273 (1939).
5. Joly, M., *J. chim. phys.*, **35**, 285 (1939); *Biochem. et Biophys. Acta*, **2**, 624 (1948).
6. Nutting, G. C., and Harkins, W. D., *J. Am. Chem. Soc.*, **62**, 3155 (1940).
7. Gibbs, J. W., "Collected Works," vol. I, p. 309, New York, Longmans, Green & Co., 1928.
8. Wilson, R. E., and Ries, E. D., *Colloid Symp. Monograph*, **1**, 145 (1923).
9. Preston, W. C., and Richardson, A. S., *J. Phys. Chem.*, **33**, 1142 (1929).
10. Burcik, E. J., *J. Colloid Sci.*, **5**, 421 (1950).

11. Trapeznikov, A. A., *Acta physicochim. U.R.S.S.*, **13**, 265 (1940); *J. Phys. Chem. (U.S.S.R)*, **14**, 821 (1940).
12. Dupré, A., *Ann. chim. phys.* [4], **7**, 406 (1866); **9**, 328 (1866).
13. Rayleigh, J. W. S., *Proc. Roy. Soc. (London)*, **48**, 363 (1890).
14. Marangoni, C., *Nuovo cimento* [3], **3**, 97 (1878).
15. Gibbs, J. W., "Collected Works," vol. I, p. 301, New York, Longmans, Green & Co., 1928.
16. Mensbrugghe, van der, *Mêm. Acad. Roy. Sci. Belgique*, **43** (presented in 1878, published in 1882).
17. Rayleigh, J. W. S., *Proc. Roy. Soc. (London)*, **47**, 281 (1890).
18. Bikerman, J. J., "Surface Chemistry for Industrial Research," p. 10, New York, Academic Press, 1948.
19. Addison, C. C., and Elliott, T. A., *J. Chem. Soc.*, **1950**, 3096, 3103.
20. Rayleigh, J. W. S., *Proc. Roy. Soc. (London)*, **29**, 71 (1879).
21. Addison, C. C., *J. Chem. Soc.*, **1943**, 535.
22. Quincke, G., *Ann. Physik* [3], **35**, 580 (1888).
23. Bartsch, O., *Kolloid-Z.*, **38**, 177 (1926).
24. Donnan, F. G., *Chemistry & Industry*, **42**, 892 (1923).
25. Shorter, S. A., *Phil. Mag.* [6], **27**, 718 (1914).
26. Rebinder, P. A., *Bull. Acad. sci. U.R.S.S., Classe sci. chim.*, **1936**, 639.
27. Neville, H. A., and Hazlehurst, T. H., *J. Phys. Chem.*, **41**, 545 (1937).
28. Schütz, F., *Nature*, **139**, 629 (1937).
29. Durney, H. A., and Patrick, W. A., Abstracts of 119th Meeting, Am. Chem. Soc., p. 5G (1951).
30. Edser, E., "4th Report on Colloid Chemistry and Its General and Industrial Applications," London, Brit. Assoc. Advancement Science, p. 263, 1922.
31. Foulk, C. W., *Ind. Eng. Chem.*, **21**, 815 (1929).
32. Rehbinder (Rebinder), P., and Trapeznikov, A., *Acta physicochim. U.R.S.S.*, **9**, 257 (1938).
33. Brady, A. P., and Ross, S., *J. Am. Chem. Soc.*, **66**, 1348 (1944).
34. Clark, N. O., "A Study of Mechanically Produced Foam for Combatting Petrol Fires," p. 87, London, Dept. Sci. Ind. Research, 1947.

10. SEPARATION BY FOAM

Section 103. The theory of foam outlined in section 98 implies a difference in the chemical composition between the surface layer and the bulk of solutions capable of foaming. This difference has been repeatedly demonstrated by experiments conducted on foams. If only one molecular or ionic species is present as solute, its concentration in the foam generally is different from that in the original or the remaining solution; this represents *accumulation in foam*. If there are several ionic or molecular species in mutual equilibrium, some of these species may be concentrated in foam preferably to the others; this is *shift of equilibrium in foam*. If the solution contains several independent constituents, foam may contain first an excess of one of them, then, after removal of this portion, an excess of another, etc.; this is *fractionation by foam*.

The same kind of apparatus is used for all these variants of the separation by foam. Two examples of the instruments generally employed are pictured in Figs. 42 and 43. In the first, the liquid is kept in a round-bottom flask, and carbon dioxide is introduced into it through a Chamberland-Pasteur filter candle. The foam formed rises in a 3-meter-long glass tube and finally reaches the conical flask shown at the left; the contents of this flask are analyzed at appropriate moments. This instrument was constructed by Gray and Stone[1] and a similar "foam tower" was employed by Perri and Hazel[2]. The second example shows a circulating arrangement[3]. Gas passes upward through the horizontal porous septum seen near the bottom of the column and the liquid layer on the septum. The foam rises in the double funnel T whose internal wall is perforated. The liquid exuding from foam runs through the perforations into the jacket of the funnel and from there back to the space just above the septum; samples of this liquid can be taken for analysis by turning the stopcock in the side tube. Other fractionating columns have been described, for example, by Abribat[4], Dognon[5], and Arrazola[6].

Section 104. If an apparatus such as depicted in Fig. 42 or 43 is employed for measuring the *accumulation* of a solute in foam, then

the gas serving for bubble formation should be saturated with the solvent before it reaches the porous septum or candle. Otherwise the solute (assumed to be nonvolatile) accumulates in foam also because of evaporation of the solvent. This difficulty proved so serious that

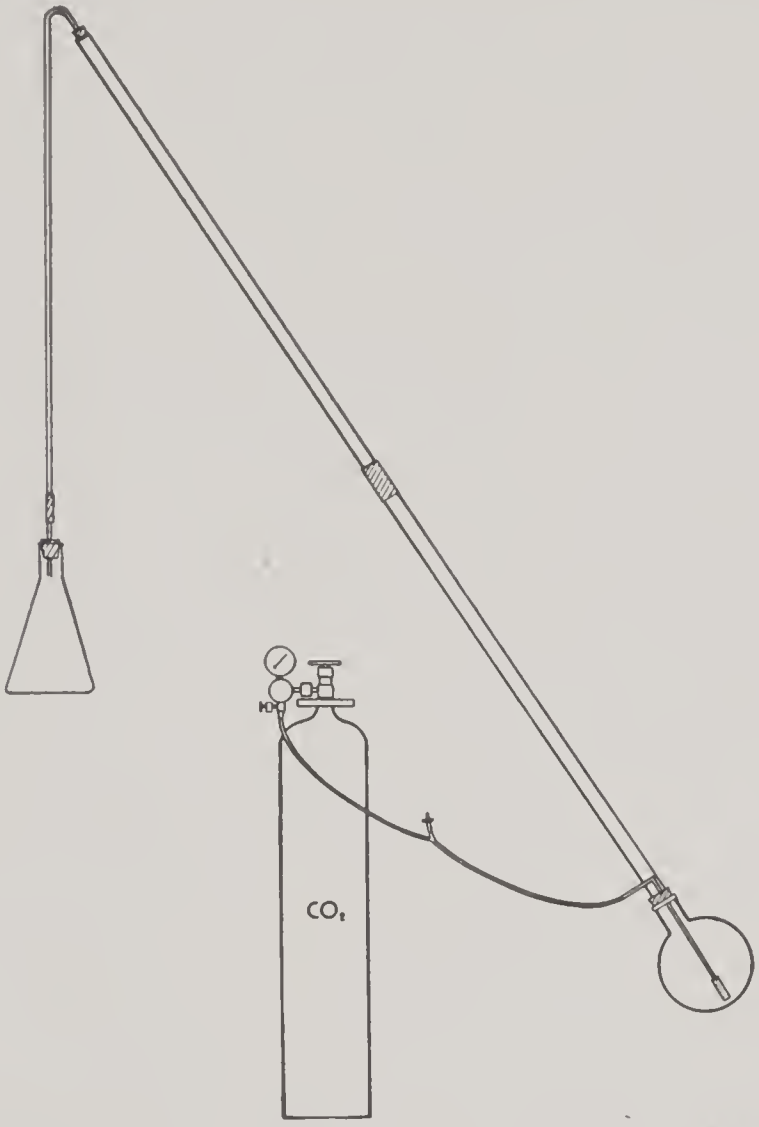


FIGURE 42. "Foam tower" for separation by frothing. From *Wallerstein Lab. Commun.*, **3**, 159 (1940).

both Zawidzki[7] and Chatalan[8] finally abandoned the pneumatic method and produced foam by shaking the liquid in an air-tight flask. A 1.29 per cent solution of saponin thus gave a foam which after draining for three days contained 1.35 per cent of saponin. After a week's drainage the degree of accumulation (i.e., concentration in foam divided by the initial concentration of liquid) was 3.5[7]. It was surprisingly small and also poorly reproducible. Presumably

the amount of solution still present in the Plateau borders was so large that the high concentration of saponin in the films was masked by its low concentration in the liquid veins.

Protracted drainage of foam to raise the degree of accumulation is

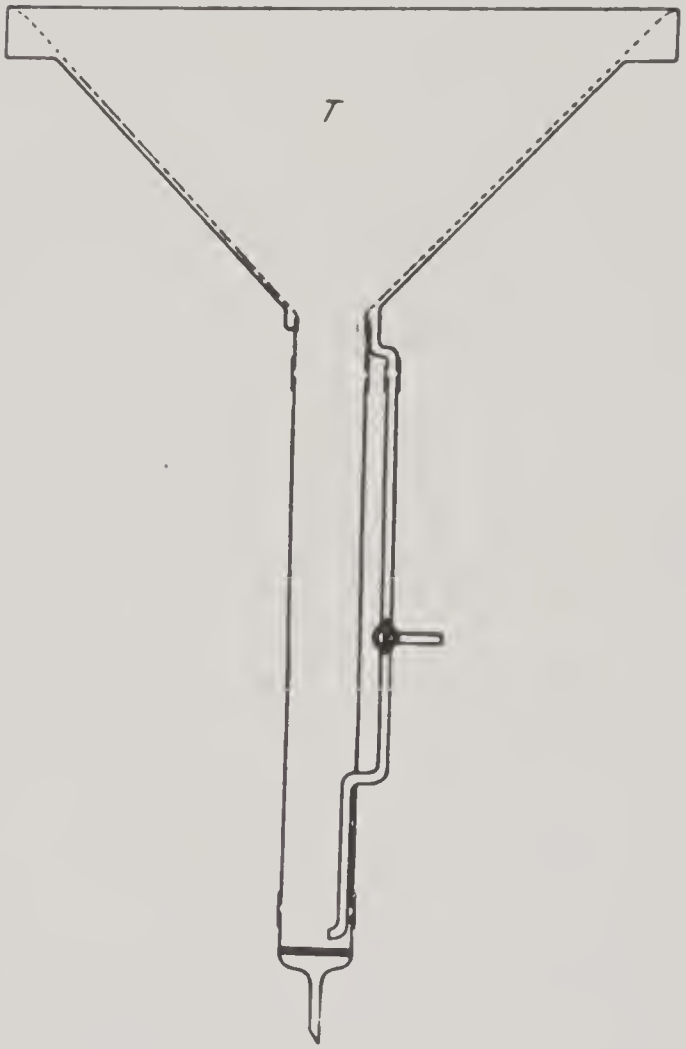


FIGURE 43. An apparatus for continuous separation by foaming. From *Kolloid-Z.*, **90**, 17 (1940).

impossible with froths as short-lived as those of aqueous amyl alcohol. Hence the concentration rise from 4.00 per cent in original solution to 4.09–4.24 per cent in foam, as found by Benson[9], is perhaps as great as can be expected. No accumulation was observed in the foam of 0.001–0.2 per cent isoamyl alcohol solutions[10]. The lather of a 2 per cent sodium oleate solution was found to contain 48 per cent more soap than the original liquid[11].

If a solution containing saponin and an electrolyte is frothed, the

froth has a higher concentration of the electrolyte than the original solution independently of whether the electrolyte raises or lowers the surface tension of pure water (i.e., in the absence of saponin)[12, 8]. Apparently, saponin in some manner carries the electrolyte along into the surface layer.

Egg white foam is more concentrated than the liquid exuding from it. Thus foams contained 2.0 to 2.3 per cent nitrogen when the exudate had 1.5 to 1.6 per cent nitrogen[13].

Accumulation in foam of nonaqueous solutions also was observed. The froth of benzene solutions of several cellulose esters had an excess of the solute although the surface tension of the solutions was almost identical with that of the solvent[14]. The original was not consulted, and it is not known how much the results were influenced by evaporation.

Section 105. The *shift of equilibrium* in the surface layer is amenable to thermodynamic treatment (see, e.g., ref. 15). Let the chemical equation of the reaction be $kA + lB \rightleftharpoons mC + nD$. Let the concentrations or, more correctly, the activities of the four reactants be denoted by $[A]$, $[B]$, $[C]$, and $[D]$. Then the change in free energy associated with the process leading from the mixture in which the ratio $\frac{[A]^k[B]^l}{[C]^m[D]^n}$ is x to the equilibrium mixture in which $\frac{[A]^k[B]^l}{[C]^m[D]^n} = K$, K being the equilibrium constant, is $RT \ln K - RT \ln x$ in the absence of capillary forces. If the change of the ratio from x to K causes change of surface tension from γ_1 to γ' and if $d\gamma/dx$ is assumed constant in this range, then in the presence of capillary forces the change in free energy is $RT \ln K - RT \ln x + S(\gamma' - \gamma_1)$, S being the area of the interfaces per gram-molecule. Let x be equal to the new equilibrium constant K_1. Then $RT \ln K_1 = RT \ln K + S(\gamma' - \gamma_1)$. Hence

$$\ln \frac{K_1}{K} = \frac{S}{RT}(\gamma' - \gamma_1) \tag{51}$$

The new equilibrium constant K_1 is greater than the constant (K) in bulk, that is, the equlibrium is shifted to greater concentrations of A and B if surface tension is lowered by A and B more than by C and D, i.e., if $d\gamma/dx$ is negative. Then γ_1 is less than γ' and the right-hand side of equation (51) is positive. The value of $\gamma' - \gamma_1$ will rarely

be greater than 10 g/sec^2. The value of RT at room temperature is about 2.5×10^{10} g cm^2/sec^2. Hence $\ln \frac{K_1}{K}$ usually will be less than 4×10^{-10} S. However, when only the surface layer is considered, S is very large and a marked change in the equilibrium constant is possible.

Section 106. The first quantitative experiments on the shift of equilibrium seem to be due to Perrin[16]. Unfortunately their description is very short. Air was forced through a 0.2 per cent soap solution. The froth after collapsing was acid, while the residue was alkaline and had surface tension about twice as great as that of molten froth. Soaps of rosin and of gamboge behaved similarly. For a froth of sodium oleate the total surface of the films was found by multiplying the average surface of a bubble with the number of bubbles (equal to number of bubbles per minute times the number of minutes). The amount of oleic acid in the froth divided by the surface area gave the surface concentration of the acid. It corresponded to a layer 1.7 to 2.1×10^{-7} cm thick.

The ratio of acid to base in the foam of sodium oleate solutions varied in the same direction as this ratio in the solution, but was greater in the froth[17]. Thus the froth contained neutral soap when the solution was $0.047N$ in respect to sodium ion and $0.042N$ in respect to oleate ion. When the solution was $0.05N$ as regards both Na^+ and oleate, the composition of the solid in the froth could be formulated as 1 mol. sodium oleate plus 0.61 mol. oleic acid. The foam contained less water than the original solution; in otherwise equal conditions the accumulation of solid was greater from acid and alkaline than from neutral soap solutions. No error caused by the carbon dioxide of air was introduced as the gas phase of the foam consisted of nitrogen. In more dilute sodium oleate solutions than those studied by Laing, the hydrolysis of soap in foam was more marked[18]. Thus the molecular ratio of oleic acid to sodium hydroxide in the froth of $2 \times 10^{-4}N$ solution was 2.7 (corresponding to sodium oleate + 1.7 mol. oleic acid) while in the froth of $10^{-2}N$ to $1.6 \times 10^{-2}N$ solutions it was 1.5. When the froth of a solution more dilute than $2 \times 10^{-3}N$ was redissolved in the residual liquid, the surface tension of the product, contrary to expectation, was not equal to (was greater than) the surface tension of the original solution. Perhaps this obser-

vation demonstrates that chemical reactions in soap solutions are rather slow.

The molecular ratio of base to acid in the foam seems to be little sensitive to the chemical nature of the base. An aqueous liquid containing 0.125 per cent lauric acid was mixed with alkali solutions so that the base:acid ratio was 0.91 for sodium hydroxide, 1.12 for triethanolamine, and 1.28 for potassium hydroxide. In the foam of the resulting soap solutions this ratio was 0.79, 0.89, and 1.05, respectively. In all three instances the surface tension of the residual liquid was about 1.25 times that of the molten foam[19].

The froth of green 0.02 per cent bromothymol blue solutions is yellow while the residual solution is blue[19a]. This may be another example of the shift of equilibrium in the surface layer.

It is clear that chemical analysis of a foam which still contains large percentage of the original solution cannot directly give the composition of the surface layer. If the amount of water in the froth is determined and it is assumed that the liquid in the lamellae has the composition of the initial liquid, then the amount and composition of the surface films can be calculated. Apparently this calculation has not yet been carried out. Also no further attempt, after Perrin, has been made to correlate the degree of hydrolysis with the extent of the surface.

Hydrolysis in foam might be useful in chemical analysis. Foaming of 0.4 per cent solution of sodium cholate yielded crystals of pure cholic acid in one of the foam fractions[20].

Section 107. *Fractionation* by foam has been extensively studied and there were attempts to utilize it in industry. It can serve, for example, for purifying a compound from its surface-active impurities, for isolating a surface-active compound from its mixture with inactive substances, and for finding the compound responsible for the foaming capacity. In fractional distillation, signal to start a new fraction often is given by a rapid rise in temperature. In fractional frothing, it is advisable to begin a new fraction when the foam height rapidly decreases (or increases) at a constant rate of air flow[21]. Usually such a change of foam height is indication of a change in the composition of the frother, but it can be caused also by mere change in concentration. Thus if the starting solution was more concentrated than the solution having maximum foaminess (see, e.g., section 34),

its foaminess increases during frothing because of the removal of the frother with the froth, and this increase may be somewhat sudden if the maximum of the foaminess-concentration curve is sharp.

Commercial dodecyl sulfonic acid and sodium dodecyl sulfate were purified by frothing[22]. The acid had a minimum of surface tension (about 34 g/sec^2) in 0.007 *M*. The foam of this solution, after dilution to 0.007*M*, had surface tension γ of about 29 g/sec^2, and the residue had γ 41 g/sec^2 at this concentration and showed no minimum of γ in the concentration range studied. The sodium dodecyl sulfate solutions before frothing showed a minimum of γ (about 24 g/sec^2) also at 0.007 g-mol./1. The foam fraction had γ of about 22, and the residue had γ of about 39 g/sec^2 at the same dilution. There was no minimum on the γ-concentration curve of the residual liquid.

Section 108. The efficiency of separation by foaming can be expressed in several manners. If, for example, N_1 is the mole fraction of the surface-active ingredient in the solution, the solvent being disregarded, N_1' the corresponding fraction in the froth, and N_1'' in the residue, then N_1'/N_1 may be called *lesser coefficient* of fractionation, and N_1'/N_1'' *greater coefficient* of fractionation. If the molecular weights (or some of these) are not known, weight fractions can be used rather than mole fractions. The solvent must be disregarded as accumulation without fractionation is not intended in these experiments. Thus, if the solution consists of a g-mol. of A, b g-mol. of B, c g-mol. of C, and s g-mol. of solvent, then N_1 of component A is $a/(a + b + c)$ rather than $a/(a + b + c + s)$. If x per cent of component A originally present in solution is finally found in foam, then xN_1'/N_1 may be termed *degree of separation;* this again can be based either on mole fractions and mole per cents or on weight fractions and weight per cents.

Section 109. Two fatty acids sometimes can be partly separated by frothing solutions of their alkali salts. Thus when 100 g water containing 0.1 g sodium oleate and 0.1 g sodium laurate were foamed with nitrogen and the fatty acids mixture was isolated from the foam, this mixture contained 60 per cent oleic and 40 per cent lauric acid, while the mixed acids obtained from the residual solution had only 19 per cent oleic acid[23]. Thus the lesser coefficient of fractiona-

tion (see section 108) was (in weight units) 1.2 and the greater coefficient, 3.2. As sodium laurate solutions have at 45° a lower, and at 90° a higher surface tension than sodium stearate solutions of equal dilutions, preferential accumulation in foam of laurate at lower and of stearate at higher temperatures could be expected. This expectation was confirmed by Dubrisay.

Partial separation of oleic from stearic and palmitic acids succeeds if strongly alkaline solutions of the potassium soaps of these acids are frothed at about 50° or sodium soap solutions are frothed at 75° [24].

A striking example of fractionation by foam is afforded by separation of two dyes of widely different hues. Patent Blue (a triphenylmethane dye carrying a hydroxy, two diethylamino, and two sulfo groups) is in aqueous solution a better frother than Scarlet Red (also known as New Coccine, Ponceau 4 R, etc.; an azo dye carrying a hydroxy and three sulfo groups). When a violet solution of both Patent Blue and Scarlet Red is frothed, the foam is blue and the residual liquid is red. The efficiency of separation depended on the relative amounts of the two dyes. When nitrogen was bubbled for 10 min. through 100 cm^3 of solution containing 0.01 per cent Blue and 0.01 per cent Red, 3.5 cm^3 of collapsed foam and 96.5 cm^3 residue were obtained. The concentrations in foam were 0.225 per cent Blue and 0.02 per cent Red, and in residue 0.003 per cent Blue and 0.01 per cent Red. Thus for Patent Blue the two coefficients of fractionation (in weight units) were 1.8 and 4.0, respectively. The degree of separation was about 130. All these values are approximate only because the final amounts of the dyes do not exactly add to the initial amounts. It is not clear how far these results[3] were affected by evaporation. When the starting solution contained 0.92 per cent Blue and 0.04 per cent Red, nitrogen had to be bubbled for 60 min. to remove the main part of the Blue. The foam yielded 96 cm^3 of liquid having 0.94 per cent Blue and 0.04 per cent Red, while the residual liquid (4 cm^3) had 0.77 per cent Blue and 0.04 per cent Red. The lesser coefficient of fractionation for Patent Blue was just above 1.0, showing that separation of a large amount of surface-active material from a small amount of inactive substance is not feasible by frothing. When the surface-active component is present in a relatively small amount, its removal is easy. When nitrogen was bubbled through a solution of 0.008 per cent Blue and 1.05 per cent Red, the foam was 0.025 per cent in respect to Blue and 1.08 per cent in respect to Red, and the lesser coefficient of fractionation was 3.0.

Section 110. In this and the two following sections froth fractionation of complex mixtures of unknown composition is reviewed.

Fatty acids and bile acids present in commercial bile preparations can be separated by frothing[20]. When 0.4 to 0.5 per cent solutions of the commercial sodium salt were foamed, the bubble persistence gradually decreased and the rate of nitrogen flow had to be increased to force the bubbles over the highest point of the "foam tower" (section 103). During this stage fatty acids and their soaps were removed with the foam. Then the persistence suddenly rose. The more stable foam obtained after his change was rich in bile acids and their salts. Of the two main bile acids one (taurocholic) does and the other (glycocholic) does not contain sulfur. Two fractions of the foam collected during the second stage were analyzed for sulfur. The earlier one had 0.82 per cent sulfur and the latter, 4.21 per cent, while the sulfur content of the original preparation was 1.10 per cent. Thus, glycocholic acid is foamed away before taurocholic acid. The pH of the residual liquid increased from, for example, 6.5 to 8.5 during the foaming. To transfer a considerable portion of the bile acids into the foam it was necessary to acidify the liquid from time to time.

It is unknown what substances or organisms accumulate in the sea foam but this foam consumes 3 to 20 times as much oxygen as the equal amount of sea water, and its biological oxygen demand is 10 to 20 times as great[25].

Section 111. Removal of frothers present in the beetroot juice would greatly simplify the beet-sugar manufacture as just the substances causing froth (proteins, resins, etc.) usually prevent or retard crystallization of sucrose, which is the main goal of the manufacturing process. Both laboratory experiments[26, 27] and large-scale attempts[28] on purifying sugar juice by frothing have been recorded.

Removal of proteins from potato juice did not succeed when nitrogen was bubbled through the liquid. However, froth made with carbon dioxide was richer in protein (0.6 per cent) than either the starting solution (0.06 per cent) or the residue (0.02 per cent). As 350 cm^3 of the original solution yielded only 320 cm^3 residue and 20 cm^3 foam (after collapse), about 10 cm^3 water must have evaporated. Hence, in the absence of evaporation the protein concentration in the foam would have been 0.4 per cent ($= \frac{0.6 \times 20}{20 + 10}$ %). When then

carbon dioxide was passed through 300 cm^3 of the residual liquid until only 275 cm^3 remained, the protein concentration of this second residue was as low as 0.009 per cent[26]. The increase in stability of protein foam achieved by substituting carbon dioxide for nitrogen is in agreement with the observation by Clark and Ross (see section 50).

Fractionation by foam of a partly hydrolyzed soybean protein gave the following results[2]:

	Metaprotein	Protein	Proteose	Peptone	Amino Acids
Foam	2.5	26.3	23.8	23.7	23.7
Residue	0.0	6.1	25.6	34.1	34.2

The figures mean the percentages of the total nitrogen found in the corresponding fraction. Accumulation of metrapotein and protein fractions in the foam makes it probable that foaminess is caused mainly by these substances. Foam fractionating of apple proteins was carried out by Davis *et al.*[29]

The liquid resulting from collapse of *beer* foam is enriched in nitrogen. Thus 7500 cm^3 of beer containing 0.064 per cent N gave 1175 cm^3 foam fraction with 0.082 per cent N, while the N concentration in the residual liquid was 0.060 per cent[1]. The nitrogen in foam is not the amino-N whose concentration in froth is less than in the original beer, but rather the protein nitrogen[30]. Polypeptides of low molecular weight, which are not coagulated by heat, do not accumulate in foam which removes above all proteins precipitable by tannin or heat[31, 32]. The protein fraction preferentially transferred into foam has also been identified with albumoses[33]. In addition to protein, hop resins also are extracted by foam. The above mentioned foam fraction[1] contained 0.048 per cent resin as compared with 0.017 per cent in the original beer and 0.010 per cent in the residue. The concentration of iron (but not the total ash content) was greater in foam than in the original beer[32]. The foam fractions give foams whose rate of drainage are slower than those of the residue or the beer; thus constant k in equation (11) (section 55) was 0.006 sec, 0.012 sec, and 0.009 sec, respectively, for these liquids[1].

Section 112. Foaming can be used to purify enzymes. If the activity of the original preparation is accepted as unit activity, i.e., the rate of reaction as accelerated by 1 g of dry original specimen is set equal to one, then activities greater than one indicate a higher

concentration of the enzyme in the solid obtained. Nitrogen was bubbled through 0.5 per cent solution of commercial diastase. The diastatic activity of the foam solids was 1.48 and of the dried residue, 0.94. When 1.28 per cent solution of commercial pancreatic lipase was frothed with nitrogen until foam formation ceased, the collapsed foam contained only 1.26 per cent solids but the activity of this solid was 1.49. The sample of lipase used had two maxima of foaminess at pH 1.7 and pH 4.5. It was suspected that the first maximum was due to an impurity. This suspicion was confirmed by frothing crude lipase at a pH near 1.7; in this experiment the activity of the froth solids was less than that of the original sample[34].

Foam fractionation assisted in purifying choline-esterase from horse serum; also in this instance the foam contained more of the inactive substance than the original liquid[35].

Highly purified (crystalline) pepsin has strong rennin activity, and it has been debated for a long time whether or not pepsin and rennin are identical. The problem apparently was decided by foam fractionation[36]. 0.4 per cent solutions of commercial pepsin in 0.01*M* citrate buffer at pH 1.7 to 2.0 were frothed at 30°. The pepsin activity was concentrated in the foam 3.3 times, and the rennin activity only 1.3 times. A second foaming of the collapsed froth gave concentration factors of 7.4 and 2.6, respectively. Thus pepsin is different from, and is more surface active than, rennin.

For concentrating the gonadotropic hormones present in the urine of pregnant women the following procedure was employed[37]. Nitrogen was passed through 100 cm^3 of filtered and slightly acid urine. The residue was inactive. The upper part of the froth was removed (after 15 to 45 min. frothing) and, after collapse, subjected to foaming in a smaller apparatus. The collapse of the second foam yielded 1 cm^3 of turbid liquid which was as active as 10 to 20 cm^3 of the original urine. As thus only 10 to 20 per cent of the initial activity was recovered, the major part of this activity was lost in the process.

The bacteriophage activity can be concentrated in foam[38]. Accumulation of bacteria in foam also is mentioned here although bacteria presumably should be considered a third phase, and foaming of their suspensions results in flotation (see Chapter 13) rather than in fractionation by foam. *Escherichia coli* which has a relatively "hydrophilic" surface cannot be accumulated by frothing its suspensions in water, but it is removed with froth from a suspension in saturated aqueous solution of sodium chloride; apparently something

like "salting-out" takes place. *Mycobacterium tuberculosis* which has a waxy coat is transferred into froth also from distilled water although the transfer from 5 per cent sodium chloride solution is more rapid[5].

References

1. Gray, P. P., and Stone, I., *Wallerstein Lab. Commun.*, **3**, 159 (1940).
2. Perri, J. M., and Hazel, F., *Ind. Eng. Chem.*, **38**, 549 (1946).
3. Ostwald, Wo., and Mischke, W., *Kolloid-Z.*, **90**, 17 (1940).
4. Abribat, M., *Compt. rend.*, **209**, 244 (1939).
5. Dognon, A., *Rev. sci.*, **79**, 613 (1941).
6. Arrazola, J. M., *Ion (Madrid)*, **2**, 119 (1942); *Chem. Abs.*, **37**, 1301 (1943).
7. von Zawidzki, J., *Z. physik. Chem.*, **42**, 612 (1903).
8. Chatalan, J., *J. chim. phys.*, **20**, 123 (1923).
9. Benson, C. C., *J. Phys. Chem.*, **7**, 532 (1903).
10. Ostwald, Wo., and Siehr, A., *Kolloid-Z.*, **76**, 33 (1936).
11. Prosch, W., *Z. deut. Öl- u. Fett-Ind.*, **42**, 449 (1922); *Chem. Abs.*, **16**, 3551 (1922).
12. von Zawidzki, J., *Z. physik. Chem.*, **35**, 77 (1900).
13. Barmore, M. A., *Colo. Agr. Expt. Sta., Tech. Bull.*, **9** (1934).
14. Lee, S., *J. Soc. Chem. Ind. Japan*, **40**, *Suppl. binding*, 459 (1937); *Chem. Abs.*, **32**, 1924 (1938).
15. Thomson, J. J., "Application of Dynamics to Physics and Chemistry," p. 236, London, Macmillan & Co., 1888.
16. Perrin, J., *Ann. phys.* [9], **10**, 180 (1918).
17. Laing, M. E., *Proc. Roy. Soc. (London)*, **A109**, 28 (1925).
18. Raison, M., *Research (London), Suppl. Surface Chemistry*, **1949**, 187; *Compt. rend.*, **232**, 1660 (1951).
19. Dubrisay, R., and Drouot, P., *Compt. rend.*, **196**, 1392 (1933).
19a. Thiele, H., *Kolloid-Z.*, **118**, 172 (1950).
20. Bader, R., and Schütz, F., *Trans. Faraday Soc.*, **42**, 571 (1946).
21. Schütz, F., *Trans. Faraday Soc.*, **42**, 437 (1946).
22. Brady, A. P., *J. Phys. & Colloid Chem.*, **53**, 56 (1949).
23. Dubrisay, R., *Compt. rend.*, **194**, 1076 (1932).
24. Aenlle, E. O., and Fernandez, S. G., *Anales fis. y quím., Ser. B.*, **44**, 191 (1948); *Chem. Abs.*, **42**, 7549 (1948).
25. Skopintsev, N. A., *Compt. rend. acad. sci. U.R.S.S.*, **18**, 53 (1938); *Chem. Abs.*, **32**, 8855 (1938).
26. Ostwald, Wo., and Siehr, A., *Kolloid-Z.*, **79**, 11 (1937).
27. Spengler, O., and Dörfeldt, W., *Z. Wirtschaftgruppe Zuckerind.*, **92**, 279 (1942); *Chem. Abs.*, **37**, 6923 (1943).
28. Meyer, W., *Centr. Zuckerind.*, **48**, 449 (1940); *Chem. Abs.*, **36**, 5375 (1942).
29. Davis, S. C., Fellers, C. R., and Esselen, W. B., *Food Technol.*, **3**, 198 (1949).
30. Lüers, H., Geys, K., and Baumann, A., *Z. ges. Brauwesen*, **43**, 185, 193, 201 (1920); *Chem. Zentr.*, **1920** IV, 481.
31. Krauss, G., and Harreis, F., *Wochschr. Brau.*, **57**, 33 (1940); *Chem. Abs.*, **36**, 214 (1942).

32. Nissen, B. H., and Estes, C., *Am. Soc. Brewing Chemists, Proc.*, **1940**, 23; *Chem. Abs.*, **35**, 3029 (1941).
33. Mischke, W., *Kolloid-Z.*, **90**, 77 (1940).
34. Ostwald, W., and Mischke, W., *Kolloid-Z.*, **90**, 205 (1940).
35. Bader, R., Schütz, F., and Stacey, M., *Nature*, **154**, 183 (1944).
36. Andrews, G., and Schütz, F., *Biochem. J.*, **39**, LI (1945).
37. Courrier, R., and Dognon, A., *Compt. rend.*, **209**, 242 (1939).
38. Ruska, H., *Kolloid-Z.*, **110**, 175 (1948); *Chem. Abs.*, **43**, 4337 (1949).

11. THREE-PHASE FOAMS

Section 113. In three-phase foams, coalescence of bubbles is prevented or retarded by solid bodies partly immersed in the liquid. To understand the presumable mechanism of this effect some knowledge of the wetting of solids is needed (see, e.g., sections 10 and 11).

In section 11 it was implied that the solid was immobile and the liquid-air boundary moved over its surface. When the solid is mobile, spreading of liquid over it means that the solid is pulled into the liquid and no solid-gas surface remains. When the solid is mobile and the wetting is only partial, the solid may stop in the liquid-air interface. This occurs when equation

$$W = l\gamma \cos \beta \tag{52}$$

is satisfied. In it W is weight of the solid particle minus weight of the displaced liquid, l is the perimeter of the particle along the three-phase boundary, γ is surface tension of the liquid, and β is the angle made by the liquid at the solid with the vertical (see Fig. 44). This figure shows that the obtuse angle (φ) made by the solid and the upward vertical is $\beta + \theta$, i.e., $\beta = \varphi - \theta$. As $\cos \beta$ is greater the smaller β, the upward force due to surface tension increases when $\varphi - \theta$ decreases. As a rule, particles readily remain in the liquid surface if their wettability is poor (θ is large). At a constant θ, those particles are more readily retained in the surface which are oriented so that $\varphi - \theta$ is small. If, for example, $\theta = 90°$, particles having horizontal facets (for which φ is about 90°) have a better chance to float than particles having no such facets.

Section 114. Suppose now that a gas bubble rises and comes in contact with a solid particle suspended under another gas bubble (see Fig. 45). In analogy to the statement in section 113, it may be said that the particle is prevented from falling into the gas bubble underneath it by the force $l\gamma \cos \beta$. The physical meaning of the phenomenon is perhaps made clearer by stating that the decrease in the energy of gravitation, achieved when the particle descends, is cancelled by the increase in surface energy due to the unavoidable

distortion of the bubble shape. The contact angle valid for the climbing of the gas-liquid boundary along the solid surface is the receding angle (see section 11), which is always smaller than the equilibrium angle (unless both are zero). This means that the gas-liquid boundary nearly hugs the falling solid. If, for example, this boundary should reach the vertical faces of the particle shown in Fig. 45, it would

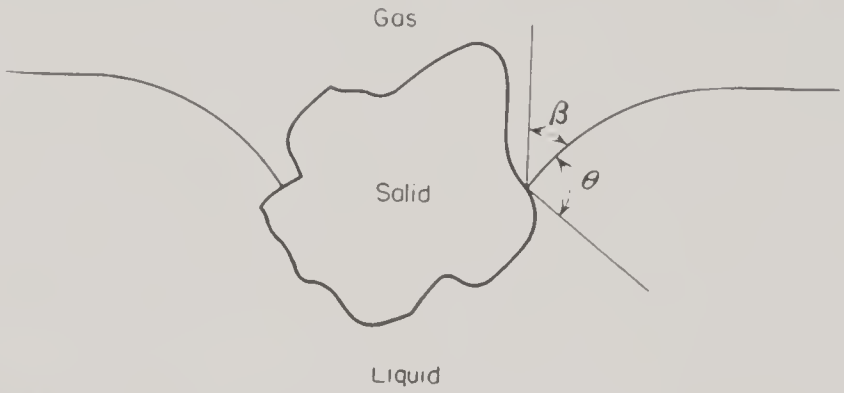


FIGURE 44. A solid particle in the surface of a liquid. θ is the angle between the liquid and the solid surfaces. β is the angle between the liquid surface and the vertical.

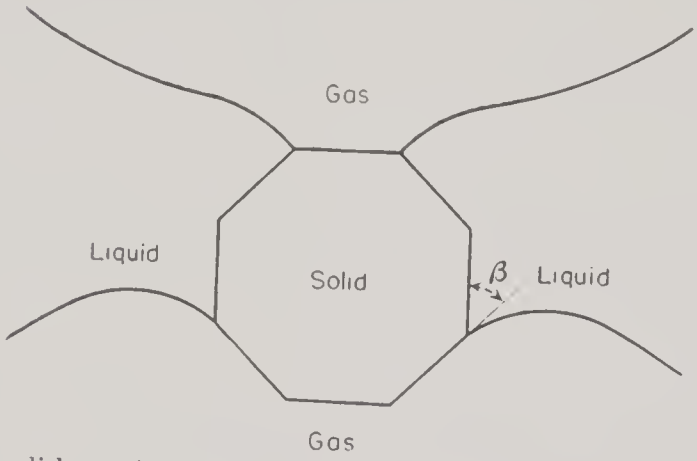


FIGURE 45. A solid particle preventing coalescence of two bubbles.

rise up almost vertically, then turn to the horizontal, and go down to reach the bottom of the bubble, which thus would become heart-shaped. The increase in surface energy associated with this shape change may be greater than the gain in the gravitational energy. Let the particle have the volume of 0.001 cm^3 (i.e., be about 0.1 cm in every direction) and the mass of 0.001 g. If it descends by one-half its length, i.e., by 0.05 cm, the gain in gravitational energy is $981 \times 0.001 \times 0.05 = 0.049$ g cm^2/sec^2. As γ of water is 72 g/sec^2, increase of the water surface by 0.0007 cm^2 would offset this gain.

Thus a solid particle tends to prevent coalescence of two bubbles if it is in simultaneous contact with the gas phases of both bubbles. Presumably, some medium degree of wettability (i.e., a medium wetting angle θ) is most advantageous. If θ is too great, the submerged fraction of the particle is too small, and the liquid partition between two bubbles will thin too far before the second end of the particle emerges in the second bubble and the specific protection afforded to three-phase foams starts to operate. If θ is too small, the particle may be completely sucked into the liquid and leave the partition with the outflowing fluid, when the film thins. Presumably, also some medium particle size is best for foam stability. Too large particles are heavy and thus too little affected by capillary forces. Too small particles, similarly to particles having large θ, would start being operative when the partition is too thin. The thinner the film, the smaller probably will be the effect of solid particles on its stability.

The theoretical conclusions mentioned in the previous paragraph remain hypothetical because the experimental material pertaining to three-phase foam is exceedingly scanty. A large volume of publications is available on flotation (see Chapter 13), but students of ore dressing paid but little attention to the stability and other properties of the foams they used.

Section 115. As mentioned in section 34, solutions of isoamyl alcohol (3-methyl-butanol) exhibit a maximum of the time of collapse (t) after shaking, which was observed, for example, at the concentration of 0.32 per cent (w/v), the t being 17 sec. The same author[1] shook aqueous isoamyl alcohol solutions with finely powdered chalcopyrite. There was again a maximum of t, and the corresponding concentration (0.3 per cent v/v) was near that observed in two-phase foams, but the value of t (60 sec) was high. The difference between 60 and 17 sec is a measure of the additional stability conferred by the solid particles. Powders of galena, sphalerite, or molybdenite increased t to several minutes. In agreement with the conclusions of section 114, the efficiency of a solid was small for both coarse (diameter greater than 0.03 cm) and very fine (colloidal) powders. The minerals studied had maxima of efficiency in the sieve range between 9,000 and 12,000 openings on a square centimeter, which presumably corresponded to the range of particle diameters between 0.005 cm and 0.006 cm.

The expected maximum of stability at some medium degree of wettability seems to manifest itself when oleic acid is added to a mixture of galena and 0.25 per cent (v/v) aqueous isoamyl alcohol[1]. If x is the final molarity of oleic acid and H is the height of froth after standard shaking, the following table can be made up:

x	0	10^{-5}	5×10^{-5}	10^{-4}	3×10^{-4}	5×10^{-4}	10^{-3} g-mol./l.
H	11	13	11	8	3	2	1 cm.

Small additions of oleic acid lower the wettability of minerals by aqueous solutions. Apparently the wettability achieved in $10^{-5}M$ solution is best for the stability of three-phase foams.

It is doubtful whether the mechanism described in section 114 is operative in the stabilization of gelatin foams by finely dispersed metal hydroxides[2]. Thus standard bubbling of air through 0.1 per cent gelatin solution gave rise to a foam column 17 cm tall which collapsed to 3 cm within 40 min. The analogous collapse (from 17 to 3 cm) required 60, 57, and 48 min. when the gelatin solution contained 0.03 per cent ferric hydroxide, 0.03 per cent aluminum hydroxide, or 0.018 per cent aluminum hydroxide, respectively. These hydroxides have been prepared by passing ammonia over the surface of suitable iron and aluminum salt solutions. Colloidal hydroxides were more efficacious. The time of collapse t was 90 min. for 0.001 per cent addition of ferric hydroxide sol, 60 min. for 0.0008 per cent chromium hydroxide sol, etc. Greater additions of hydroxide flakes or colloidal hydroxides lowered t. Thin films of copper sulfide, lead sulfide, or zinc sulfide lowered t, while colloidal sulfides raised it.

Section 116. The carry-over (priming) of boiling solutions (see section 33) sometimes is influenced by the presence of solid particles. However it is not known whether these act in virtue of their forming three-phase foams or simply because they contain gases which act as nuclei for water vapor. The latter explanation well accounts for the observation[3] that almost any powder dropped into a boiling solution (0.5 per cent sodium chloride + 0.005 per cent sodium hydroxide was used) increased priming, while no powder was active after spending some time in the boiling liquid. Only the rate of attainment of the inactive state was different for different substances; this rate was least for galena, greater for limestone, still greater for dolomite, etc. The first explanation also can be reconciled with the

facts, if we assume that galena surface slowly becomes well wettable by water if kept in hot aqueous solution, and that limestone and dolomite surfaces change in the same direction but more rapidly.

The results of some other experiments[4, 5, 6, 7, 8] are not conclusive. Perhaps the amount of air occluded by the powders or the condition of their surfaces could not be reproduced.

References

1. Bartsch, O., *Kolloidchem. Beihefte*, **20,** 1 (1924).
2. Mokrushin, S. G., *Kolloid. Zhur.*, **12,** 448 (1950).
3. Foulk, C. W., and Whirl, S. F., *Ind. Eng. Chem.*, **26,** 263 (1934).
4. Foulk, C. W., and Brill, H. C., *Ind. Eng. Chem.*, **27,** 1430 (1935).
5. Foulk, C. W., and Ulmer, R., *Ind. Eng. Chem.*, **30,** 158 (1938).
6. Durov, S. A., *J. Applied Chem. (U.S.S.R.)*, **13,** 693 (1940).
7. Leaf, W. B., *et al.*, *Am. Ry. Eng. Assoc.*, **45,** *Bull.* **441,** 58 (1943).
8. Harvey, E. N., McElroy, W. D., and Whiteley, A. H., *J. Applied Phys.*, **18,** 162 (1947).

12. FIRE-FIGHTING FOAMS

J. M. Perri

National Foam System, Inc.,
West Chester, Pa.

Section 1. The idea of the use of foam as a fire-extinguishing medium originated in the early 1900's. The first recorded attempts indicate that Laurent[1] extinguished a naphtha fire by application of foam generated by the reaction of two aqueous solutions. One contained aluminum sulfate and the other sodium bicarbonate plus saponin. The solutions were pumped simultaneously through separate lines and permitted to react in a chamber immediately prior to contacting the burning surface. The principles involved in the formation and application of this so-called "chemical foam" have not been altered appreciably to this day. From a chemical standpoint the subsequent advances in the art consisted primarily in the development of improved foam stabilizers to be used with the acid and carbon dioxide liberating chemicals.

The first use of hand fire extinguishers containing chemical foam is reported as having taken place in England in 1912[2].

Meanwhile petroleum tank farms adopted fire protection systems based upon the use of stored solutions in the manner of Laurent. In 1925 Urquhart developed means for introduction of a foam powder mixture directly into a water stream. The advantages of storing the dry chemicals (see section 5) used in place of corrosive solutions required by the "wet" storage systems (see section 4) led to wide adoption of this method of continuous foam generation. Further advances in the art pertaining to chemical foam are of minor importance with the exception of the development of foams which resist the destructive action of alcohols (see section 10 and section 11).

The possibilities of the use of foam produced by mechanical agitation were realized by Wagener[3] in 1927. By 1935 there had been developed many practical means for "air-foam" production for both fixed and portable systems[4]. Saponin and synthetics were most prominent in use as the foam stabilizers at that time and remained so until displaced by hydrolyzed protein solutions shortly before 1940. Great impetus was given to the development of field application of hy-

drolyzed protein airfoam by the Armed Forces' requirements in World War II, and by 1947 complete fire protection systems had been designed, installed, and accepted as standard by petroleum processors for tank farms and refineries.

Section 2. It has long been established that the use of foam is the most effective means for extinguishment of flammable liquid fires of all types and sizes. The advantages of a method which provides for temperature reduction and oxygen exclusion by application of a single medium made from readily available materials became early apparent.

From a chemical standpoint it is the foam stabilizer that presents the most interest. It is usually colloidal. The natures of the ingredients employed as foaming agents in chemical and airfoams differ considerably. In the case of the former, the hydrated aluminum oxide formed *in situ* aids the organic stabilizer considerably in the formation of a suitable foam and the frother need not be potent when used in water alone. Mechanical foams require foaming agents of a different class. These should be readily dispersible in water to produce a solution which can easily be converted to foam.

Section 3. The types of foam compounds most widely found in use today are listed.

A. Chemical Foam

I. *Portable Extinguishers*
- (a) 2½ Gal—Regular and Universal (Type I)
- (b) 40 Gal—Regular and Universal (Type VI)

II. *Continuous Foam Generation*
- (a) Stored Solutions ("Wet Storage") Systems
- (b) Chemical Powders
  - (1) Single—Regular and Universal (Type III)
  - (2) Dual—Regular and Universal (Type VII)

B. Mechanical or Airfoam

I. *Low Expansion*
- (a) 6% Type (Type V)
  - (1) Regular
  - (2) Subzero Use
  - (3) Universal

II. *High Expansion*

The charges designated as "universal" are the so-called "alcohol-stable type," and will be discussed separately. The regular type charges find greatest application in the extinguishment of fires involving hydrocarbons and related nonpolar compounds and are readily destroyed on contacting the lower molecular weight alcohols and related polar solvents. Both are described in general best by a consideration of recognized specifications devised by U. S. Government[5] and the National Board of Fire Underwriters' Laboratories.

Section 4. *Two and One-half Gallon Charge* (AI(a) of section 3). The charge[6] shall consist of two reactive chemical mixtures separately packed and designated as "A" and "B". Charge "A" shall contain at least 0.3 lb of powdered aluminum sulfate which will react rapidly and completely with the "B" charge to produce a strong closely knit heat-resistant foam. The "B" charge shall contain a minimum of $1\frac{3}{8}$ lb of sodium bicarbonate plus suitable foam stabilizers and preservatives. Ordinary requirements are that this charge when used with approximately 2 gal of water give a minumum foam volume of 18 gal. A satisfactory commercial type should yield 22 to 24 gal.

Fire testing of the foam is accomplished by subjecting it to a burnback test[6] or using it in the extinguishment of a standard fire[7]. The burnback test is conducted in a steel pan having dimensions 12 x 12 x 6 in. A 2-in. depth of foam is placed on 0.5 gal of gasoline floated on water, a 3-in. x 12-in. section is cut away and after 5 min. the exposed gasoline is ignited. "The foam blanket shall completely cover not less than one-half the fuel surface after the fire has burned 8 min. and shall provide an effective seal to fuel vapors during this time." This type of test is used in the testing of all types of chemical foam charges listed. The Underwriters' Laboratory test appears to be the more critical from a practical standpoint since it is based upon determining the actual fire extinguishing ability. The test fire involves 2 gal of gasoline floated on water in a tank having a diameter of 4 ft. After burning for 20 sec the foam stream from the extinguisher is directed in a standard manner across the backboard. The fire shall be extinguished with one charge. The foam must have a satisfactory degree of fluidity to fulfill the extinguishment requirements. The more rigid types of foam generally are found wanting even though they pass the burnback test.

Forty Gallon Foam Charge (AI(b) of section 3). In essence this charge is similar to that described above, however of sufficient quantity to

be used with about 33 gal of water. The minimum foam volume requirements are 225 gal[6] and 250 gal[7]. Commercial charges yield 350 to 400 gal of foam from a single charge. No standard fire test exists; however, a foam of the proper fluidity extinguishes a 10-ft x 10-ft gasoline fire readily.

The nature of the extinguishers dictates the necessity of using charges which are completely soluble in water and remain so during the period of storage. Chemical sediment formation or organic growth seriously interferes with operation of the extinguisher and constitutes an extreme hazard to operating personnel since pressures are likely to be developed that exceed the strength of the extinguisher.

"Wet" Storage Charges—Fixed Systems (AII(a) of section 3). As in the case of the 2½ gal extinguisher, solutions of "A" and "B" chemicals are stored separately and are mixed when the foam is needed. These charges vary in size from the small automatic tip-over devices used to protect dip tanks to solution storage tanks of many thousands of gallons from which the solutions flow by gravity or air pressure or are pumped simultaneously. The stabilizer is usually provided in liquid form for easy addition to the sodium bicarbonate solution. Inasmuch as these solutions are likely to stand for years the problem of solution maintenance arises. It is usually found that the "B" solution gradually becomes deactivated, the bicarbonate being converted to carbonate. Restoration to its full utility can be accomplished by passing carbon dioxide through the solution until a pH of 8.0 to 8.5 is achieved. Normally 8 volumes of foam are obtained from 1 volume of combined solutions.

Section 5. *Chemical Powders* (AII(b) of section 3). The single powder type is usually contained in a 50-lb package and consists of the usual "A" and "B" components plus agents designed to confer proper flow characteristics and keeping qualities to the powder. In the early stages of the development of such powders it had been found that "caking" occurred on storage. This was probably due to a reaction occurring between the closely associated bicarbonate of soda and aluminum sulfate, a reaction being induced by moisture. A simple test has been devised in the field to determine whether chemical that has been in storage for a long time has deteriorated. The closed container is simply inverted and tapped on the bottom; a "caked"

material will give a dull response in contrast to a metallic ring indicating satisfactory material. Present-day formulation and manufacturing procedure, however, have overcome this shortcoming. Being a powder it is likely to "pack" and make for difficult handling when needed.

JAN-C-267 specifications[6] concerning foam volume for these generator powders require that each pound of powder yields one cubic foot of foam when used with specified equipment. In practice, with standard commercial equipment under normal conditions, 10 to 16 volumes of foam are obtained for each volume of water depending upon the design of the system. The type of foam that is obtained from the single powder may range from the too fluid to the too rigid type. The conditions necessary for the achievement of a foam of optimum fluidity and maximum fire resistance have been developed on a purely empirical basis and existing chemical foam installations lack flexibility as a result. The most important of the factors influencing foam quality are water temperature and extent of resistance that the foam encounters in the hose of pipelines. It is known from a qualitative standpoint that the lower water temperatures delay the chemical reaction, hence the length of pipeline necessary to contain the reactants until the foam is fully developed also varies. A factor which places further limitations on the extent to which chemical foam may be permitted to flow through pipelines is the ease with which it breaks down when subjected to mechanical stress.

Section 6. *Mechanical Foam Liquids* (B of section 3). Mechanical foam came into general use in the United States during World War II. The demands of the Armed Forces for a simplified means of making fire-fighting foam led to development of a mechanical foam liquid using hydrolyzed soybean protein as a base. A few years later products derived from fish scale, hoof and horn meal, and peanut and corn proteins came onto the market. The characteristics of this type liquid are best described by reference to the partial list in Table 10, of the U. S. Government Specifications JAN-C-266[5]. The foam liquid is introduced into the water line by various means at a 6 per cent concentration; air is then introduced to yield a foam consisting generally of 90 volumes air, 9.4 volumes water, and 0.6 volume foam liquid.

TABLE 10. CHARACTERISTICS OF MECHANICAL FOAM LIQUIDS

Characteristic	JAN-C-266 Specification	Regular 6% Type	3% Type	Subzero Type
Specific gravity @ 60°F	1.120 min.	1.125	1.175	1.102
Viscosity @ 20°F (centistokes)	100 max.	43	90	40; (300 @ −20°F)
pH @ 70°F.	6–7.5	7.1	7.0	7.4
Pour point (°F)	15 max.	5	−18	−25
Sedimentation (% volume)	0.1 max.	0.02	0.01	0.01
Precipitation in 6% solution				
Fresh water	0	0	0	—
Sea water	0	0	0	—
Aging	No change	No change	No change	No change
Foam volume @ 70°F (gal foam/gal liquid)	125	135	—	—
Expansion	—	—	10	10 (7.5 @ −20°F)
Fire requirements				
Coverage (minutes)	2 max.	1	1	1
Control (minutes)	4 max.	2	2	3.6
Extinguishment (minutes)	5 max.	2.5	2.5	4.0
Foam blanket-depth (inches)	2	3.5	3.0	3.0
Sealability (minutes)	15 min.	20	20	20
Rekindling (void test)	24″ x 24″ max.	14″ x 14″	15″ x 15″	15″ x 15″

Specific Gravity. A value as indicated in JAN-C-266 provides for a protein content of 25 to 35 per cent.

Viscosity. Since in most instances the liquid is drafted through metered orifices the viscosity is of importance. Ideally the viscosity of the liquid should be independent of temperature. It has been found through practical experience that the viscosity of the liquid may approach 300 centistokes before the decrease in rate of liquid introduction is sufficient to affect appreciably the quality of the foam.

Aging. The aging test is conducted in part by subjecting the liquid to a temperature of 150°F. for 24 hours. Improperly prepared liquid usually develops nonhomogeneity as evidenced by "skin" or sediment formation. Sediment formation in excess of 0.1 per cent would indicate that the liquid would be susceptible to sediment formation on aging.

Foam Volume. The specifications call for the use of the standard NPU nozzle (U. S. Navy Specifications) which has a capacity of 60 gpm at 100 psi. The expansion obtained is 8 to 9 as compared to approximately 10 for the same liquid through commercial foam nozzles.

Fire Tests. The fire tests are conducted on a 10 ft × 10 ft gasoline fire applying foam produced from water pumped at a rate of 6 gpm. The foam stream is directed through the fire to the far wall of the test tank. A foam must have

proper degree of fluidity (see section 13) lest the continuity of the foam blanket be disrupted in a manner as to permit separation along vertical planes. As a result, the gasoline surface will be re-exposed and difficultly covered again since the surrounding foam has drained considerably and flows freely no longer. The covering quality of the foam is tested 15 min. after the extinguishment of the fire by passing a lighted torch over the foam blanket to determine whether ignition will occur through the foam. After the blanket has aged 15 min. a 6 in. × 6 in. square is cut, and the gasoline is ignited and permitted to burn for 5 min. The void shall not increase to an area greater than 24 in. × 24 in.

Section 7. The same fire test equipment has been used to advantage in evaluation of foam liquids according to the minimum quantities or rates of application necessary to achieve extinguishment within a given time. Thus it has been found that foam made from the 3 per cent liquid described above extinguishes the standard fire when applied at two-thirds the rate specified in JAN-C-266. Another favorable feature of this test is its suitability for evaluating directly the factors that others had attempted to measure indirectly and on a small scale. A qualitative picture of the flame resistance is obtained by observation of the behavior of the foam stream as it passes through the fire. The resistance to radiant heat (see section 16) is measured by the coverage time (see section 6) and viscosity (see section 13) by the control time (see section 6). Stability toward gasoline (see section 15) is measured by the sealability test (see section 6) and burnback (see section 4) by the void test (see section 6).

Section 8. The experience gained through the above test has helped in devising a smaller scale test that serves equally satisfactorily and has been used in Underwriters' Laboratories' evaluation of new foam liquids[8]. The test pan measured 5½ × 5½ × 1 ft. The foam was applied through a manifold having four outlets placed at one corner of the tank and directed down the tank wall. The rate of water-in-foam application was varied from 0.04 to 0.16 gpm/sq ft at 100 psi using the JAN-C-266 test nozzle by simply adjusting the position of the outlets on the manifold so that only the required amount of foam was delivered into the test tank. The introduction of foam was started at the lowest rate and increased until satisfactory extinguishment was obtained.

That tests in which the rates of foam application are excessive are not sufficiently discriminatory can be demonstrated at the highest

rate of foam application[9]. Fires involving ethyl acetate, isopropyl ether, or isopropyl acetate are just as readily extinguished with protein-type foam as is a gasoline fire, although the first three solvents are notorious for their disruptive action on foam. Again, test conducted on iron-free, protein-type liquid aged 10 years showed the same extinguishment time as the iron-fortified foam at a water-in-foam application rate of 0.04 gpm/sq ft. However, at 0.0275 gpm/sq ft the rate of foam destruction exceeded the rate of application and the foam failed to extinguish the fire.

Standard fire test performance was established using gasoline as a fuel and regular 6 per cent protein foam applied at a water rate of 0.04 gpm/sq ft. The control time (see section 6) of 2.75 min. was more readily reproducible (±15 sec) than total extinguishment time and was adopted as a reference value. This test was then used to evaluate the efficacy of the protein-base liquid as an extinguishing agent for fires involving materials other than gasoline (see Table 11). For some materials two rates of application were tested.

TABLE 11. EFFECTIVENESS OF MECHANICAL PROTEIN FOAM ON VARIOUS SOLVENTS

	Gasoline		Isopropyl Acetate		Ethylene Glycol		Acetaldehyde	Ethyl Acetate		Ethyl Ether
Rate water application (gpm/sq ft)	0.04	0.013	0.04	0.093	0.013	0.04	0.16	0.16	0.22	0.133
Control time (min.)	2.75	None	None	1.75	5	2	3.5	3.5	1	3.5

In the case of isopropyl acetate it is seen that extinguishment comparable with that of the standard fire can be achieved at a rate slightly below the 0.093 indicated and for ethylene glycol at a rate between 0.013 and 0.04. The other data lends itself to like interpretation. To achieve the control time of about 2.75 min., the rate of application must increase in the following order:

Ethylene glycol
Gasoline
Isopropyl acetate
Ethyl ether
Ethyl acetate
Acetaldehyde

i.e., acetaldehyde fires are most persistent.

Section 9. The displacement by a material possessing lower surface tension of less active molecules at the surface is discussed in Chapter 3, section 47; see also ref. 10. Perri and Hazel[11] explored the same subject with reference to protein foams and alcohols. Surface film studies showed that the protein film-forming substances were readily displaced by water-soluble alcohols, the effective concentration being lower the greater the molecular weight of the soluble alcohol. A

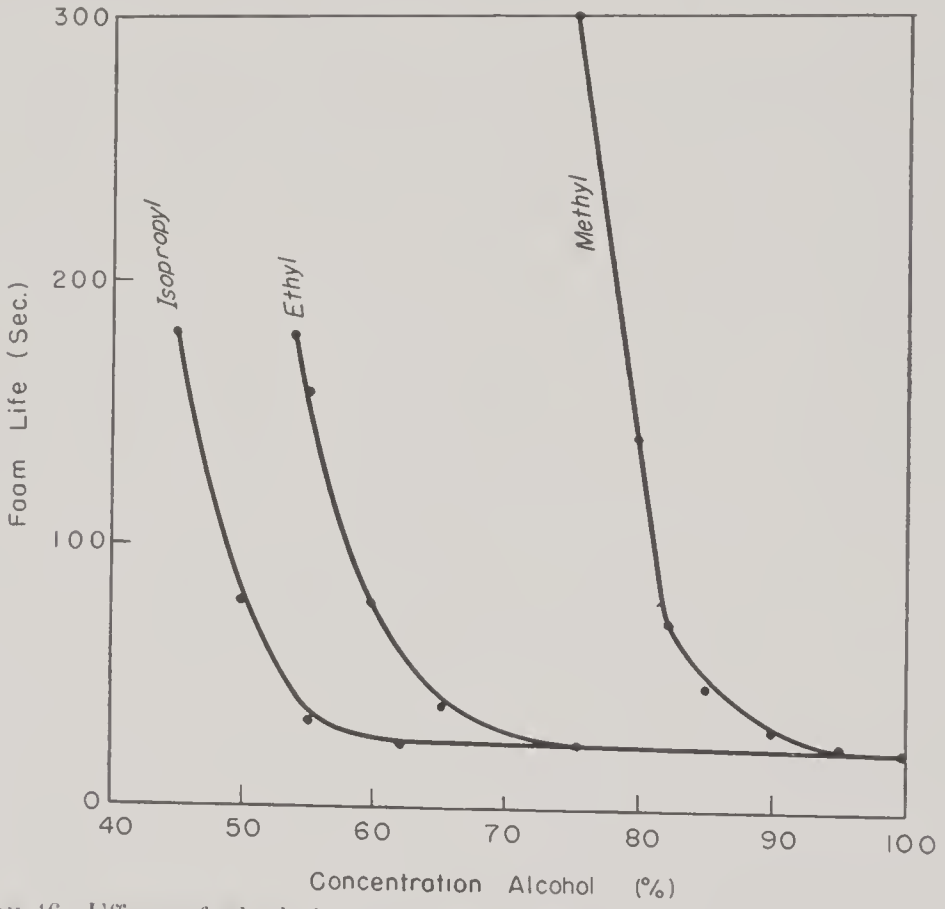


FIGURE 46. Effect of alcohols on protein foam. From Perri and Hazel[11].

qualitative picture was also obtained concerning the effect of alcohols on protein-type foam. The persistence of foam superimposed on various alcohols was measured. From Fig. 46 it is seen that the observations made in the surface film studies are borne out, the higher molecular weight alcohols being the more disruptive toward the foam studied.

Section 10. The fact that most nonhydrocarbon flammable liquids require special consideration as regards effective foam application has long been recognized. The first successful composition to be pro-

duced and used on a commercial scale derives from the Boyd patent (see section 24). Insoluble fatty acid soaps had been utilized to stabilize foam bubbles against attack by alcohol vapors. Since then stabilizers and charges have been devised for portable extinguishers[12] and mechanical foam equipment[13]. These developments consisted primarily in modifying the basic stabilizing ingredients so as to achieve compatibility with the given foam-making devices and procedures.

Tests conducted by the Underwriters' Laboratories[14] in 1940 on single-powder chemical foam (see section 3) were used as a basis for establishment of National Fire Protection Association Standards[15] for protection of alcohols. The test results in the extinguishment of 150-sq-ft fires are summarized in Table 12. The N.F.P.A. pamphlet No. 11, 1951 also recognizes the use of such foams for extinguishing fires involving the following flammable materials:

Alcohols	Acetates	Ethers	Ketones
Methyl	Methyl	Ethyl	Acetone
Ethyl	Ethyl	Isopropyl	Methyl ethyl ketone
Propyl		Amyl	
*Butyl		Dioxane	
*Diacetone		Cellosolves	
		*Carbitols	

* These represent borderline cases in which the material destroys ordinary foam to some extent. A higher than usual rate of regular foam application is necessary to achieve effectiveness ordinarily encountered on petroleum products.

TABLE 12. USE OF ALCOHOL-STABLE FOAMS ON SOME SOLVENTS

Flammable Material	Extinguishment Time (min., sec)			Rate of Application Water-in-Foam (gpm/sq ft)	
	Single Powder Chemical	Mechanical Foam (sec)	2½ Gal. Extinguisher (sec)	Single Powder Chemical	Mechanical Foam
Isopropyl ether	4 min. 25 sec	65	15	0.13	0.1
Methyl acetate	1 min. 30 sec			0.10	
Diethyl ether	8 min. 25 sec	55	26	0.27	0.2
Methanol	1 min. 30 sec	55	25	0.10	0.1
Ethanol	1 min. 7 sec	59	25	0.10	0.1
Isopropyl alcohol		49	25	0.10	0.1
Ethyl acetate	1 min. 20 sec	50	17	0.10	0.1
Acetone		45	42		0.1
Isopropyl acetate		47	16	0.10	0.1
Gasoline		60	46		0.1
Acrylonitrile		40			0.1

Test experience with alcohol-resistant foam from the 2½ gal extinguisher was reported in 1950[16]. The fire tests were conducted in the standard 4-ft-diameter test tank (see section 4). The results are incorporated in Table 12.

Section 11. The introduction and general acceptance of mechanical foam application as vastly superior to chemical foam created a need for a mechanical foam that would resist alcohol vapors. The regular protein types are indicated in the N.F.P.A. pamphlet No. 11 as unsuited for fires involving the following. This list is not considered complete and represents only current knowledge.

Alcohols	Acetates	Ketones	Ethers
Methyl	Methyl	Acetone	Ethyl
Ethyl	Ethyl	Methyl ethyl	Isopropyl
Propyl (all)	Isopropyl	Methyl isobutyl	Butyl
Butyl (all)	Butyl	Methyl *n*-amyl	Dioxane
Amyl (all)	Amyl	Acetonyl acetone	Cellosolves
Hexyl			Carbitols
Heptyl			
Octyl			
Nonyl			
Diacetone			

An alcohol-resistant mechanical foam was introduced into the field in 1951[13] and conformed in most respects to existing specifications for mechanical foam liquid. The fire tests were conducted for the most part on the 5½-ft × 5½ ft test pan previuosly described (see Table 11) to determine the minimum rates of foam application necessary to extinguish the various fires, and to make possible comparison with the "standard" gasoline fire test. The test results are included in Table 12[17].

From a chemical standpoint only two formulations may be said to be of practical significance. Although the manner of preparation of the liquid differs, both employ the same foam stabilizing principle disclosed by Boyd[46], that is, formation of an insoluble soap in the foam bubble wall. In one case[106], compatibility of the components of the heavy metal soap in an aqueous medium is achieved by sequestering the metallic ion in the form of its complex ammonia salt. Zinc or copper salts and fatty acids having 7 to 11 carbon atoms can thus co-exist in the presence of excess ammonia. The pH value of such a composition exceeds the limits generally recognized as acceptable[5].

A neutral composition[13], harmless to personnel and equipment, uses fatty acids having 12 to 14 carbon atoms. Aluminum salts and the fatty acids are incorporated into a degraded protein solution with the aid of a solubilizer of the alkyl-aryl sulfonate type.

Section 12. *Specific Gravity of Foam.* The role played by specific gravity (see Chapter 5) of fire-fighting foams has been investigated variously. In actual practice reference is made to expressions which are functions of the specific gravity. Friedrich[18] used the term *foam number*, defined as the volume ratio of foam to water. *Expansion*[19, 20], which is the reciprocal of the specific gravity, however, finds general current usage. The foam number was determined by taking a container of known capacity, filling it to overflowing with foam, and weighing it when full. Tuve[19] employed a vessel of specified dimensions. Friedrich found in a study of the five mechanical foams available in 1943 that the foam numbers varied. Some had values as high as 19, others as low as 7 and one, 10. A standard commercial branch-pipe foam applicator was used. The most desirable value was considered to be between 6 and 10.

Foam volume measurements were made by Clark[20] using a branch-pipe leading by means of piping and a trumpet-shaped deflector into a rectangular brick structure having a capacity of about 500 gal. It was found that it was most desirable to collect 400 gal of foam, as smaller quantities led to inconsistencies. Corrections were made for thermal air expansion since temperature differences between the air and water could lead to an error of 4 per cent in the foam expansion. The pressure of superimposed foam was found to be inappreciable and not further considered. The correction for the temperature coefficient of expansion factor varied little between 15 and 20°C. The general nature of the concentration-expansion curves obtained is indicated in Fig. 47. The relationship between the expansion factor and concentration of foaming agent in solution follows in all cases a proportionality up to a certain point beyond which the factor becomes seemingly independent of concentration. A mixture of ammonium isopropylnaphthalene-β-sulfonate and gelatin (see section 19) was the most copious foamer; however, the foam was not closely knit and contained many large bubbles, some 20 in. in diameter. The same was found to be true, only to a lesser degree, with a potash-coconut fatty acid soap solution, a foam expansion of about 11 being obtained

at a 2 per cent concentration. The blood hydrolysate which might be taken as representative of the protein-type liquids generally found in practice today, required higher concentrations and pressures to achieve satisfactory foam volumes. This type, however, produces a foam which generally is composed of finer bubbles and is capable of retaining its liquid content for a longer period of time. The expansion of the blood hydrolysate solutions was greatest at a pressure of 150 psi and keratin at about 125 psi.

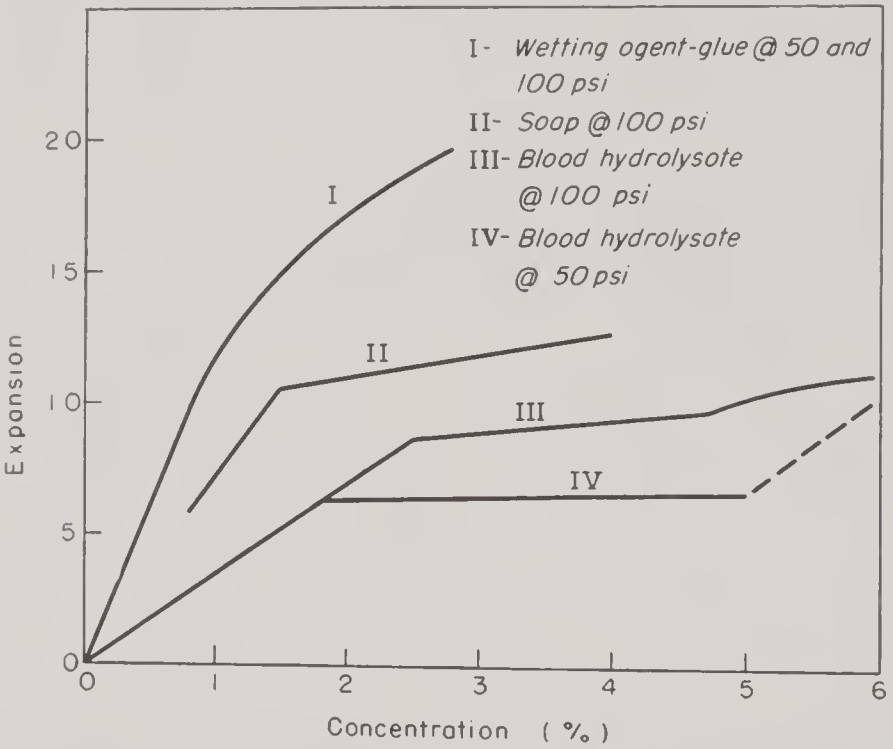


FIGURE 47. Effect of concentration of foaming agent on expansion. From Clark[20].

The effect of temperature upon the expansion of a fire-fighting foam has considerable practical importance. The data used in construction of Fig. 48 were obtained using a commercial foam nozzle and a soybean protein hydrolysate[21]. The expansion is at a maximum in the temperature range 85–90°F. Dependence of the heat resistance (see section 16) upon the expansion is also indicated.

A factor not considered in the literature is the dependence of the extent of submergence into the fuel upon the expansion. This is of concern particularly in cases where the foam is permitted to fall into the fire rather than to flow on. The more dense foam will penetrate the fuel farther and carry up with it a correspondingly greater

amount of flammable liquid, consequently subjecting a greater number of foam bubbles to direct flame attack. A high expansion foam (15 or more), on the other hand, is also found to be deficient because the extreme updrafts accompanying a fire retard direct fall of the foam. Current usage indicates that expansions of 8 to 10 are the most practical.

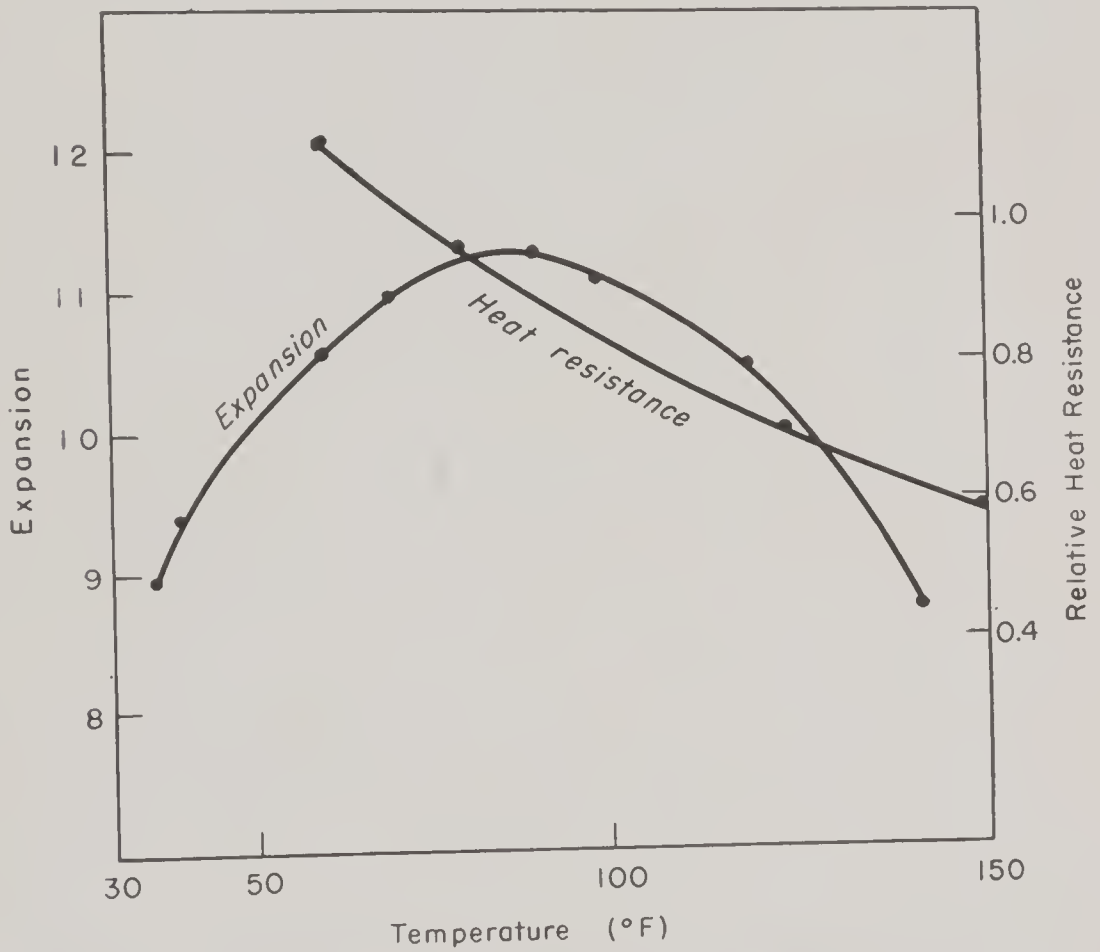


FIGURE 48. Effect of temperature on expansion of mechanical foam. From ref. 21.

Tuve[19] found that at low rates of foam application the lower expansion foams required longer periods of time to extinguish a fire. As the rate of foam application was increased the optimum expansion decreased; for example, at rate of 0.04 gpm water/sq ft, expansion of 8 is best, and at 0.2 gpm water/sq ft, expansion of 4 is best. At a rate of 0.09 gpm/sq ft, near that in current use, there was no appreciable difference in extinguishment times for foams ranging from 4 to 12 expansions. The tests were conducted on a small scale and it is indicated that the general application of the data may be limited. Tests

conducted on a 10 ft × 10 ft gasoline fire (section 6) showed that a protein hydrolysate foam having an expansion of 5 required about 8 min. for extinguishment as compared to 5 min. for a 10-expansion foam under same water rate conditions. Indications are that the governing factor was the rate of foam application, the higher expansion foam covering the liquid surface more rapidly.

Section 13. *Fluidity.* The facility with which foams spread over the surfaces of burning liquids has been investigated indirectly by consideration of foam viscosity. Difficultly controllable factors which were considered to influence fluidity in actual practice are the surface onto which the foam was applied, the age of the foam, and the temperature. Laboratory consideration has been given to the effects of type and concentration of foaming agent, temperature, bubble size, age of foam, extent of energy input into foam, density, and pressure (see also Chapter 5, section 74).

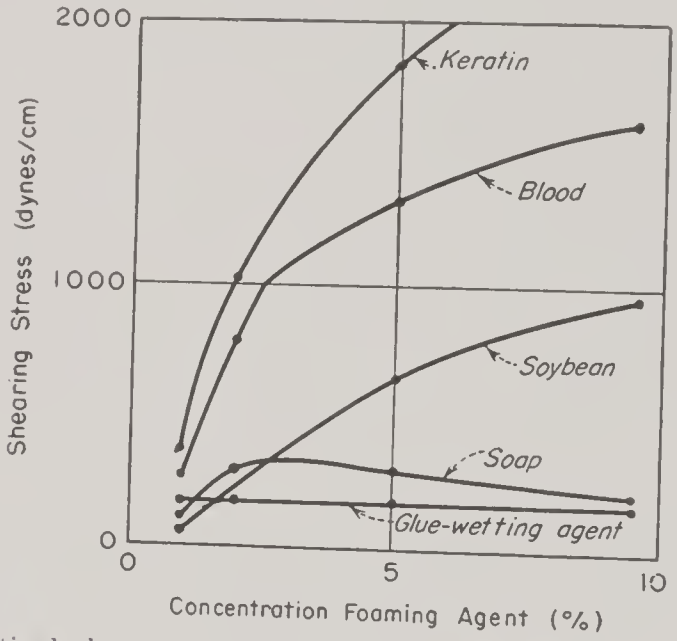


FIGURE 49. Critical shearing stress of mechanical foams. From Clark[20].

Friedrich[18] reported on the increase of viscosity with concentration of foaming agents for "Schaumgeist," "Kometextract," and "Tutogen E." These were all protein-type foams of German manufacture. The viscosities of related materials "Tutogen OL," "N," and "NW" were quite independent of concentration. No explanation is given. Amsel's foam viscometer[22] based upon resistance to upward

travel of a sphere through the foam was employed. Clark[20] found limiting shearing stress dependent upon concentration of foaming agent for the hydrolyzed proteins from keratin, blood, and soybean. At equal concentrations the foam from the keratin was most resistent, that from blood less, and soybean protein least (see Fig. 49). A glue-wetting agent mixture and a soap solution showed no appreciable change over the same concentration range considered. The hydrolyzed keratin and blood also showed increased viscosities as extent of heating increased, whereas the glue-wetting agent mixture was relatively unaffected.

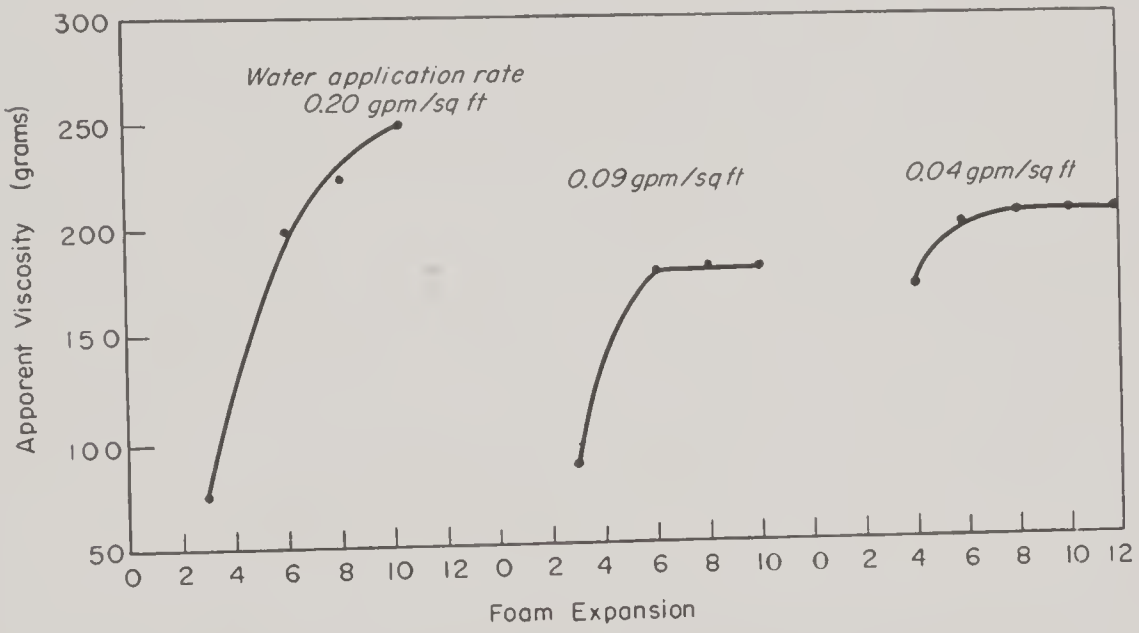


FIGURE 50. Variation in optimum foam viscosity with expansion value. From Tuve and Peterson[19].

Tuve[19] considered the influence of apparent viscosity as measured by a modification of Amsel's apparatus and water drainage on the fire-extinguishing ability of protein foams. It was found that the less viscous foams were not the most effective in extinguishing gasoline fires in spite of the rapid coverage expected. Presumably such foams lose their water rapidly and become more vulnerable to flame attack. Conversely the more viscous foams, although having lower rates of water drainage, are hindered in performance by lack of fluidity. Conclusions drawn here were based upon fire tests conducted in 22.5-in. diameter test tank. A set of curves is given indicating the optimum foam viscosities at various expansions (Fig. 50).

Interest in the viscosity of foam is also displayed quite apart from

its direct relationship to fire extinguishment. Grove *et al.*[23] investigated the effects of pressure, rate of shear, and air/water ratio on the apparent viscosity to provide data which could be used for predicting pressure drops on transporting foam in pipes. Increased pressure on the foam decreased the viscosity for the reason that the accompanying reduction in air volume gave the effect of a foam of decreased expansion. The dependence of viscosity on expansion is implied in Figure 49 after consideration of section 12.

Section 14. *Foam Stability at Ordinary Temperature.* This name was given[22] to the half-time of drainage (see Chapter 4). This is defined as the length of time required for a standard quantity of foam to yield half its liquid content. Amsel states that a foam that undergoes no considerable change in volume and retains its liquid content is undoubtedly better than one which drains off rapidly. It was recognized that the values obtained are valid only in considering foams of equal expansion values. Tuve established minimum extinguishment times on the 2.76 sq ft gasoline fire tests for foams of expansions 4 to 6 and above 8. The optimum drainage time for the lower expansion foams was longer than that for foam of higher expansion. On the basis of this work the National Fire Protection Association has adopted the procedure as part of a scheme for field evaluation of foam. A guide chart (see Fig. 51) has been prepared that lends itself to easy interpretation.

Section 15. The effect of gasoline (or other liquids immiscible with and lighter than water) upon the foam stability was measured[20] by a simple modification of the apparatus described by Foulk *et al.* (see Chapter 2). This was achieved by merely covering the surface of the foaming liquid contained in the graduated glass column with 100 cc of the immiscible liquid. Relative values show that blood and keratin hydrolysates are about the same at 110, with soap at 97 and the glue-wetting agent mixture the least stable at 93. Decreased stability was attributed to greater susceptibility to diffusion of hydrocarbon vapors into the bubble, increasing its size and internal pressure. Although this may be a contributing factor it appears that some consideration should be given to the more direct effect of physicochemical reaction. It has long been established that soap is an effective solu-

bilizer for hydrocarbons and it is to be expected that alteration of the adsorbed layer in this manner would radically change its physical characteristics. The protein is not so affected. Unpublished observations by the author lend credence to this thought. Foams which are stable on alcohol show decreased stability on alcohol containing hydrocarbons. With a sufficiently high concentration of hydrocarbons the foams are destroyed on contact. The primary foam stabilizers in

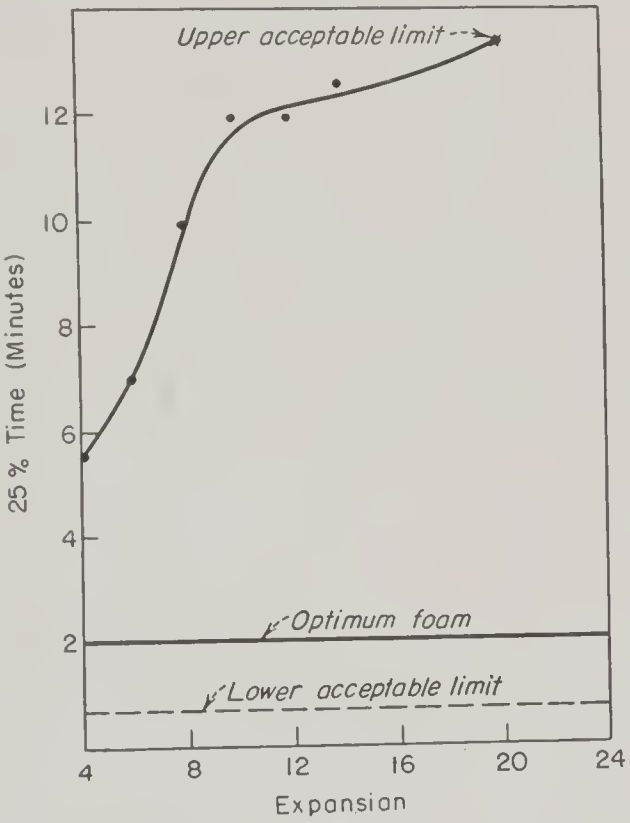


FIGURE 51. Guide for determining relative airfoam quality. "25% Time" is time required for 25% of liquid eontent to drain. After the National Fire Protection Association.

these foams are aluminum soaps (see section 24) which, as is known, are extremely more soluble in hydrocarbons than in alcohol.

A further observation concerning the interplay between soaps, hydrocarbons, and mechanical foams is of much practical interest. In the combating of spill fires involving hydrocarbons it is the established practice to attempt to "knock down" the fire instantly using a "dry chemical extinguisher" and then foam as a protective cover to prevent "flashbacks." The dry chemical extinguisher discharges a cloud of finely powdered sodium bicarbonate containing a

small percentage of aluminum stearate. Liquid hydrocarbons treated in this manner with aluminum stearate destroy protein-type foam on contact. Soap foams are relatively unaffected.

Section 16. *Stability at Elevated Temperatures.* Measurements of the heat resistance of foam were made by exposing a given quantity contained in a dish to a Bunsen burner flame[24] or by placing in an electric oven[22, 20]. Both tests measured the rapidity of foam collapse. In the former the time was taken as that required for 80 per cent decomposition and in the latter, as the time at which a clear surface became visible (see Chapter 2, section 29). Clark[20] used a simpler modification of Amsel's apparatus. In principle a quantity of foam in a calibrated vessel was exposed to overhead heat from electric heater elements of the threaded rod type. The period taken for half the foam to collapse was observed. It was found that an unfortified soybean protein foam collapsed more readily than the soap foam. The addition of ferrous sulfate, however, to the soybean protein hydrolysate has shown a reversal of this condition in practice. Protein foams in general are made more heat resistant by the addition of ferrous sulfate, the source of the protein being of secondary importance as regards this property. The degree of dispersion was found to be a factor with protein foams, heat resistance increasing as bubble size decreased. The soap foams are not so affected.

Tests conducted by the author have shown that although the soap foams are less heat-resistant than iron-containing protein foams, quicker extinguishment of a gasoline fire is obtained when the foam is applied gently at rates around 1 gpm/sq ft. A high value of heat resistance is not in itself productive of rapid extinguishment; its value lies primarily in improving the covering quality (see section 17) of a foam blanket exposed to radiant heat for a period of time.

French[26] exposed foam in glass tubes to radiant heat to determine rate of destruction. The maximum heat resistance was found in foams of low expansion and high shear strength. The heat resistance increased with an increase in water content over the normal range of expansion.

Section 17. *Covering Quality.* Friedrich[18] defined this as the ability of the foam to prevent escape of gases from a covered liquid. In this

test a diaphragm was placed at the 5 cc mark of the cylindrical test vessel into which 5 cc of gasoline was introduced. Foam was then added to a height of 15 cm above the diaphragm. The test vessel was heated slowly and the maximum pressure of the gasoline vapor was measured. This point was reached shortly before the gasoline vapors broke through the foam blanket. It is clear that the resistance of a foam column to unilateral pressure as described in Chapter 5, section 68 is measured here. Reference is made to this property also in the JAN-C-266[5] specifications for mechanical foam (see section 6 and "sealability" in Table 10). The fact that the test of this reference is conducted under actual field conditions adds to its reliability. It is clear that the property measured here primarily is that measured by Clark (see section 18).

Section 18. *Figure of Merit.* The approach taken by Clark[20] in devising a fire test was that of investigating separately the factors of production and consumption of foam. It was preferred to subject a stationary preformed foam blanket to attack by fire, since tests in which foam was permitted to flow onto the burning gasoline showed that the rate of foam consumption decreased with time as the fire intensity decreased.

Gasoline was permitted to flow under a confined 163 sq ft area of foam afloat on water at a constant rate of about 1 gpm. After approximately 5 min. the gasoline was ignited in the neighboring area contacting the foam on one edge of the blanket. The fire was permitted to burn until a standard area of foam, 27.5 sq ft, had been consumed.

Test results were converted into a *Figure of Merit* (F-M) defined as the ratio of the rate of production to the rate of consumption. The rate of production, sq ft/min., was represented by the facility with which an area of burning gasoline could be covered assuming no breakdown of foam. Variations in the F-M were noted depending upon the wind direction. With fire toward the foam the value was 60 as compared to 310 with wind in the opposite direction.

Further refinements of this test procedure are described by Fry and French[25, 26]. Provision was made to flow the foam over the gasoline surface rather than over water to obtain the rate of production. The test pan measured 8 in. x 42 in. and contained only 2 gal of fuel, which permitted testing indoors eliminating the variables of wind direction and velocity. The F-M values obtained on hydrolyzed pro-

tein, soap and wetting agents were in the same order as Clark's. It was recognized that while the F-M indicates the relative values of different materials, it cannot be used as a basis for calculating the quantity of material or the rate of application necessary to extinguish a given fire. In order to be able to use the F-M as a basis for deciding acceptability of a given foam it will be necessary to correlate the values with actual fire extinguishing tests.

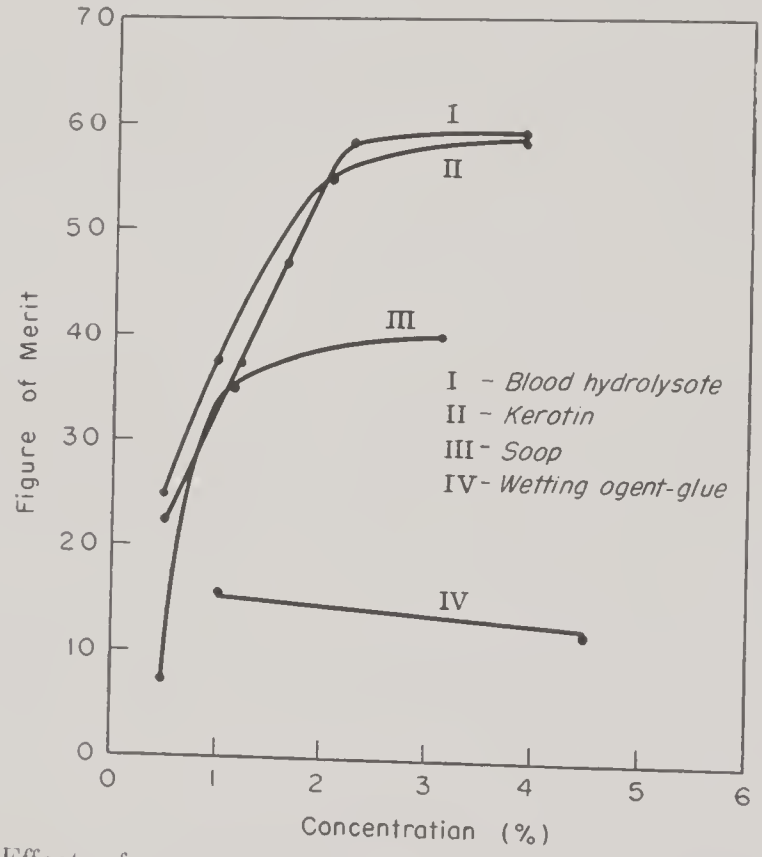


FIGURE 52. Effect of concentration of foaming agent on Figure of Merit. From Clark[20].

Clark's F-M values for various compositions are indicated in Fig. 52. All foam was made at 100 psi. At equivalent concentrations the blood and keratin hydrolysates were the more fire resistant with values of 60 and 55, being followed by soap with a value of 40 and the glue-wetting agent mixture at about 13.

Variations on the F-M with pressure at which the foam was made from hydrolyzed keratin showed that the maximum had not been achieved at 150 psi with a 3 per cent solution. At 100 psi a limit of 55 is achieved at about 2.5 per cent; at 50 psi the F-M was 30, and did not increase appreciably on up to 5 per cent concentration. The

relationship between the F-M and concentration of a foaming agent in solution follows in all cases a proportionality up to a certain point after which F-M becomes seemingly independent of concentration. A very similar function is shown by the expansion factor and concentration and there is obviously a close dependence of the F-M on the expansion factor.

Section 19. *Rating of Foams.* Amsel's[22] investigation is particularly noteworthy since it included means for rating of foams on a numerical basis. His "foam index," I, shows the relationship between heat stability, h, expansion, s, and viscosity, z, each determined as previously described.

$$I = \frac{h}{\log (sz)}$$

A number of foams evaluated in this manner were found to yield the same general order when classified by "burnback tests" (section 4). The latter tests were conducted in a 3-meter-diameter pan. Foam volumes and extinguishment times for an 18-meter-diameter gasoline fire are given along with I values. It is claimed that by knowing I for a given foam one can calculate in advance the extinguishment time for an 18-meter-diameter gasoline fire. The limitations on the usefulness of I are apparent, it being of value primarily as a means for comparing foams.

Friedrich's[18] evaluation of five mechanical foam materials in use in Germany in 1943 was done in a less rigid manner. " 'Tutogen N' and 'NW' belong together; they yield relatively high foam numbers . . . have high rate of foam delivery. Their fluidity and emulsification factors are high; their stability and blanketing power are . . . very low. . . . 'Tutogen E' differs considerably, in part, from the other products. Its foam number lies in the favorable zone; its stability and covering quality are really good. Unfortunately its fluidity varies very strongly with the concentration, aging of the foam, and temperature."

Clark's attempt to synthesize a mathematical expression correlating laboratory test data and F-M values was not successful. It was possible, however, to devise an empirical combination of factors which yielded an expression that might find application in prediction of fire test performance.

$$M = K \frac{H \sqrt[3]{R} \sqrt{t}}{FE}$$

where M = figure of merit; K = constant; H = heat resistance; R = resistance to gasoline; t = blanket thickness; F = flow under heat period; and E = branchpipe expansion. The K values for some foams are given and indicate tolerable constancy.

Compound	Concentration (%)	K
Hydrolyzed keratin	1	1.66
	3	1.80
Glue-wetting agent mixture	1	1.84
	3	1.44
Potash-coconut oil soap	1	2.16
	3	1.88
Hydrolyzed blood	1	1.60
	3	1.86

The materials investigated were those that had received some attention in actual practice at one time or another. Very conflicting reports from the field concerning relative merits of various compounds used in fighting fires necessitated investigating a large number of materials. The descriptions of the materials are given in sufficient detail to enable one to reproduce them readily. The compounds prepared may be classified as follows:

Glues—Ten per cent aqueous solutions were prepared from glues of jelly strength ranging from 70 to 200.

Hydrolyzed Proteins

(a) Blood—Whole blood was variously hydrolyzed as to heat conditions and time with ammonia or caustic soda, neutralizing agents being NH_4Cl or HCl. Ferrous sulfate was added to some as a foam stabilizer. Removal of the precipitate formed at pH of 3.6 was also included in procedure for one preparation.

(b) Keratin—Horn and hoof meal was treated with lime and neutralized with HCl or H_2SO_4 and 3 per cent ferrous sulfate added.

(c) Soybean Protein—Prepared by lime hydrolysis, acid digestion, and sulfuric acid neutralization.

Saponin—Various grades of saponin were tested, ranging from "pure" to crude concentrates, alone and in combination with hydrolyzed blood or glue.

Wetting Agents—Ten per cent solutions of isopropyl naphthalene β-sulfonic

acid and triethanolamine lauryl sulfate. Sulfonated isopropylated mineral oil containing added sodium chloride.

Soap—Potash soap of a mixture of coconut fatty acids.

Mixtures—Hydrolyzed blood and saponin; glue and saponin; glue and a wetting agent plus urea.

The first fire tests conducted by Clark cleared up considerably the confused picture presented by the previously referred to conflicting reports from the field. The hydrolyzed keratin was shown to be vastly superior to the unstabilized soap type; F-M ratings of 43 and 4.4 were obtained respectively. The rate of consumption by a gasoline fire was approximately 10 times as great for the soap foam as for the protein foam. Consideration of other properties of these foams from a laboratory standpoint revealed that although the soap foam was the more stable at normal temperature and in presence of gasoline vapor it lacked the resistance to attack by liquid petroleum fractions that protein foams possess. From this it appeared that the property of resistance to contact with liquid hydrocarbons was an important factor in the behavior of the foam in extinguishing petroleum fires. Further investigation from this standpoint revealed that saponin solutions were very stable in the presence of gasoline and improvement was noted by addition of glue. An adverse effect on the expansion of the saponin solution was noted however. No indication is given as to whether the increased stability would compensate for the loss in foam volume, although it seems unlikely that the rate of foam consumption would have decreased to such an extent as to render the mixture the more favorable. Attempts to boost the expansion factor of the mixture by addition of wetting agents were successful; the triethanolamine lauryl sulfate was used primarily. An adverse effect was again noted as a result of the addition in the form of reduced stability toward liquid hydrocarbons. The addition of wetting agents to glue solutions, however, in general improved stability in this respect. Soap destroyed entirely the resistance of the glue to liquid hydrocarbons. Important is the extent of refinement of the glue when used in conjunction with wetting agents; it appeared that neither crude nor too refined is desirable.

The above account of the unpredictable nature of the results obtained was used to demonstrate the complexity of the interactions involved and the further need for investigation of colloidal properties of the systems. The effect of additions on the superficial viscosity of solutions capable of being converted into foam which resists liquid

hydrocarbons showed that this property had some bearing. In general those wetting agents that caused a decrease in the superficial viscosity of saponin solutions also reduced the resistance of the foam to liquid hydrocarbons. Addition of hydrolyzed blood to saponin solutions increased the expansion factor, and in contrast to the wetting agents, did not appreciably affect the superficial viscosity nor resistance to liquid petroleum products. Limited variations in conditions of blood hydrolysis showed no appreciable effect. Superficial viscosities vastly superior to those of saponin solutions were created by the simple addition of certain salts to the protein hydrolysates. Soluble salts of iron, zinc, and aluminum were used to demonstrate this effect.

Solution	Superficial Viscosity Degrees of Torsion
Hydrolyzed blood, 2%	0
Hydrolyzed blood, 2% + 0.1% ferrous sulfate	335
Hydrolyzed blood, 2% + 0.1% aluminum sulfate	306
Hydrolyzed blood, 2% + 0.1% zinc sulfate	345

Chemical Foam Stabilizers

Section 20. Chemical foam as indicated before (section 1) is composed essentially of three ingredients, the acid and basic constituents plus the foam stabilizer. In the absence of the stabilizer the reaction produces a slight froth which has no utility in fire extinguishing. The stabilizers are varied, being primarily colloidal in nature and range from simple aqueous extracts of vegetable matter to complex synthetic organics. Since 1904 when Laurent[1] conducted fire tests using saponin as a foam stabilizer, a variety have been used or recommended for use. These lend themselves to a loose classification as given below.

Section 21. *Saponins and Glucosides.* In 1917 Erwin *et al.*[27] patented what they describe as a quick acting foam compound. A sodium bicarbonate solution was used to leach the foam stabilizers from powdered soap bark and further provided a source of gas for the foam. Sulfuric acid was used as the acid constituent. Because of the inability to effect complete solution of the soap bark ingredients it was necessary to stir the bicarbonate solution immediately before use. In 1924 Van Leuven *et al.*[28] patented, as stabilizers, saponin and quebracho extracts to be used in conjunction with the usual bicarbonate of soda and aluminum sulfate. Caustic soda was added to the bi-

carbonate solution to prevent the organic precipitation that ordinarily would occur. In addition to the probability of causing difficulty in operation the pasty sludge formation would detract from the "tough-

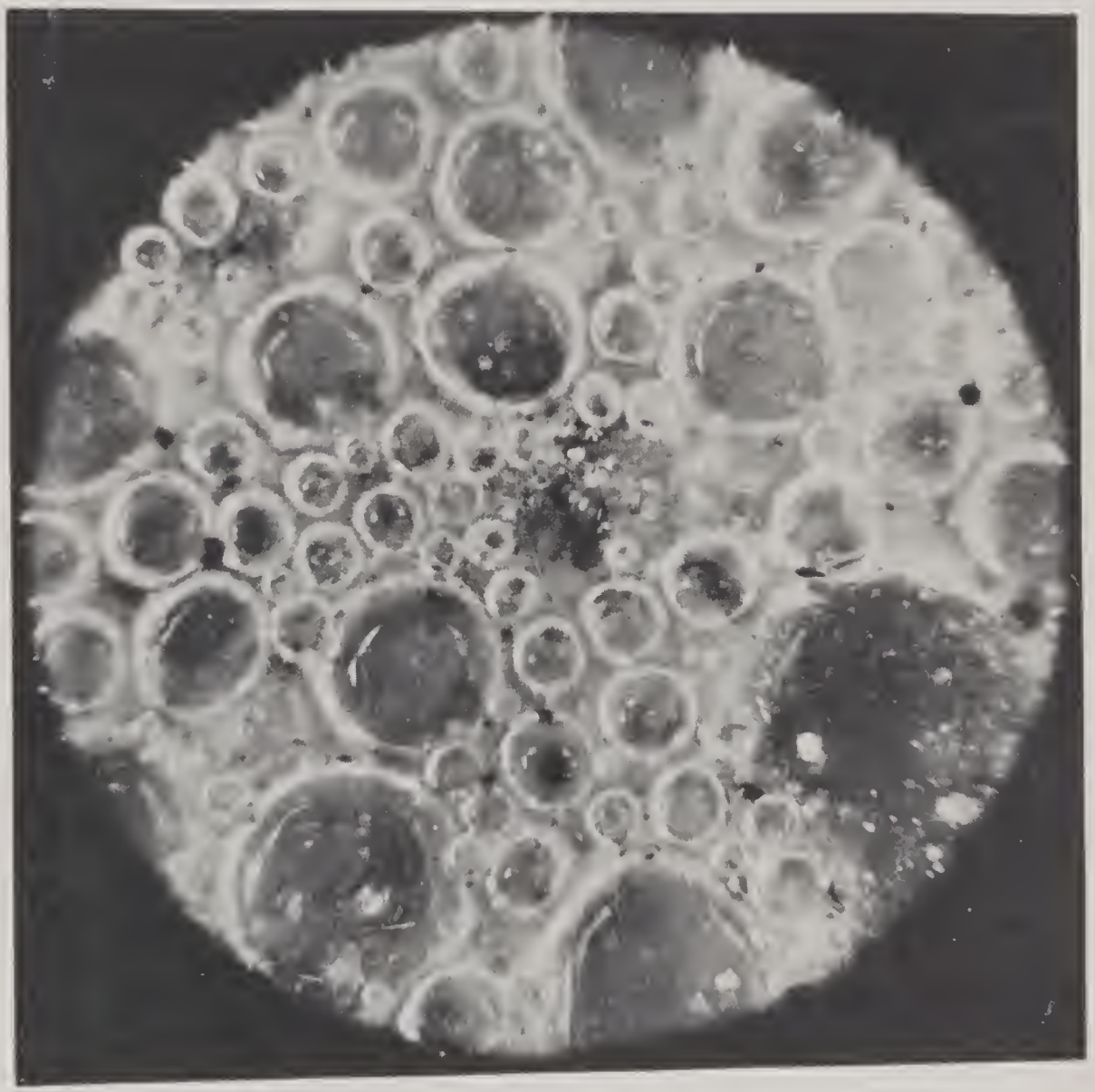


FIGURE 53. Chemical foam: soap stabilizer. Magnification ×30.

ness" of the foam. The quebracho extract is any commercial grade of so-called "reds" from tanning liquors.

The use of licorice root extracts is first mentioned by Bartels[29] in 1914 in a patent concerned with a process for extinguishing fires. This is a forerunner of the later established so-called "wet" sys-

tems (see section 4). One licorice root solution contained a "suitable" acid and the other bicarbonate of soda. These were pumped simultaneously into a mixing pot provided at the base of the oil storage tank to be protected. The solution lines may also run into the tank to provide for mixing at the oil surface or below. British patents[30, 31, 32] show the use of licorice root in conjunction with Panama bark and sulfuric acid and also alone. Thomas *et al.*[33] in 1934 used licorice root extract as the foam stabilizer for a composition containing in addition to the regularly used aluminum sulfate and sodium bicarbonate, compounds containing elements of Group I of the Periodic Table. The acetates, formates, stearates, lactates, halides, chlorates, and nitrates of K, Rb, and Cs conferred fire resistance to the foam in addition to lowering the freezing point of the solutions. A typical solution having a freezing point of $-22°$ is composed of 30 per cent potassium lactate, 8 per cent sodium bicarbonate, 2 per cent licorice root, and 60 per cent water. The acid ingredient contains chlorsulfonic acid.

A patent granted to White[34] in 1944 disclosing the use of ferric sulfate as the acid constituent includes licorice extract in the formulation. Ferric sulfate had been proposed previously but found unsuitable; however, when subjected to controlled heating and grinding it serves satisfactorily. It is claimed that when used to the extent indicated in the composition; sodium bicarbonate 42½, ferric sulfate 42½, clay 10, stabilizer 5, it is less bulky in the dry form and gives longer range foam streams than the equivalent amount of aluminum sulfate. Ferric sulfate, although used during wartime emergency, is not an item of production today. Licorice root extract was used also in conjunction with insoluble soaps (see section 24).

Section 22. *Proteins.* Proteins in various forms may be considered generally satisfactory as chemical foam stabilizers; however, the patent literature is rather sparse. In 1911 glue and glucose were patented[35]. Crosby *et al.*[36] in 1921 point out the disadvantages of the use of glue, glucose, and soap; these substances are not sufficiently fire resistant and subject to deterioration on standing in solution. Casein and other proteins which are readily soluble in sodium bicarbonate solution are claimed to be stable. The reaction with aluminum sulfate produces aluminum-protein compounds which "toughen" the foam. In 1942 Urquhart[37] patented a composition claimed to produce a

more stable foam than had been obtainable up to then utilizing the soybean. The stabilizer is produced by converting the protein to a readily soluble form by treatment with caustic soda or sulfuric acid.

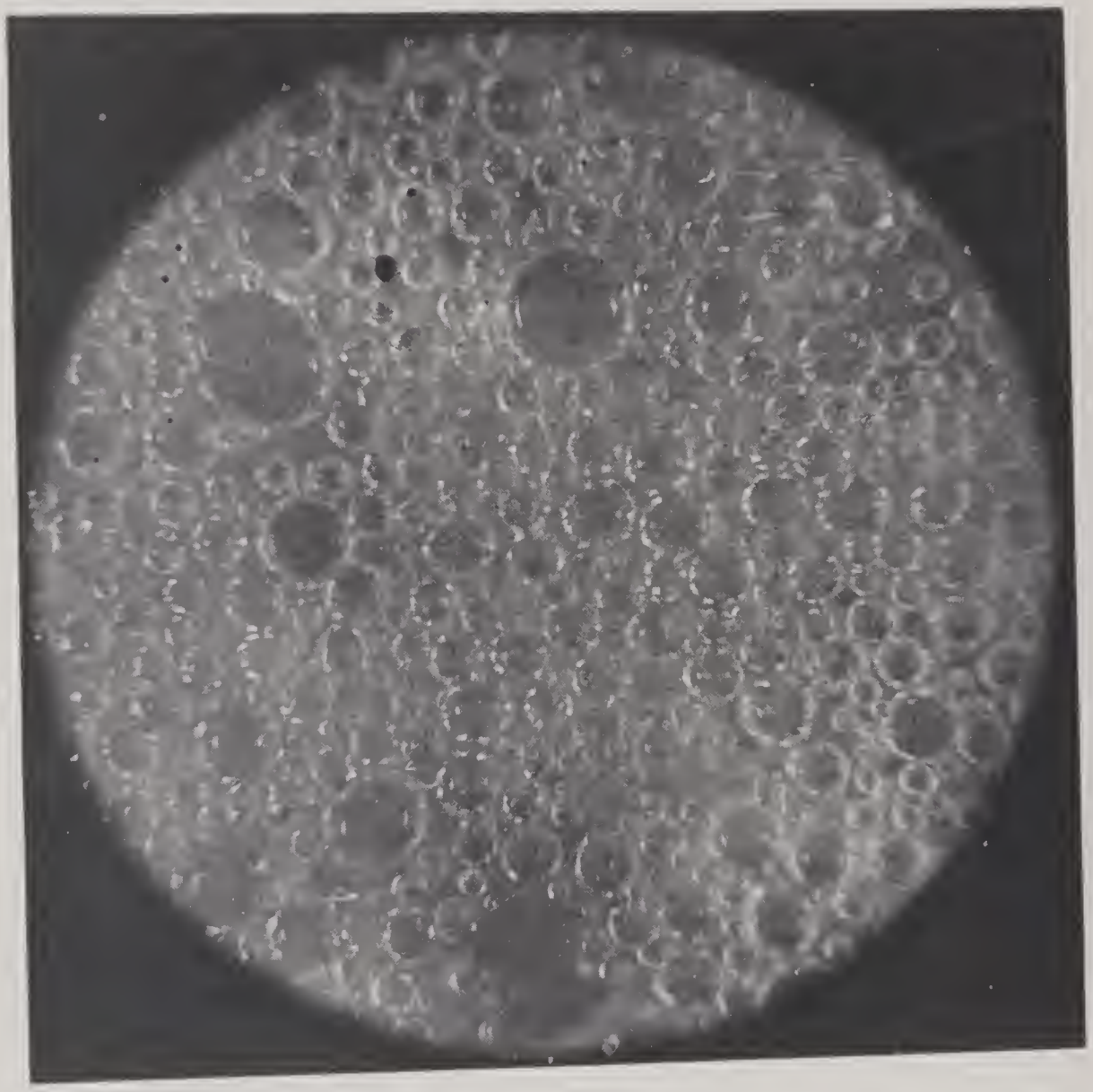


FIGURE 54. Chemical foam: protein stabilizer; very rigid foam. Magnification ×30.

Oxidation of the soybean protein by use of potassium permanganate, reaction with nitrous acid, or by digestion with oleic acid are also declared as alternate treatments. The resultant reaction products are preferably spray dried to produce a powdered stabilizer of low hygroscopicity.

Section 23. *Sulfite Liquor.* The black sulfite liquor by-product of the paper pulp processing industry is first mentioned in a 1917 patent issued to Walker[38]. The process is described wherein wood is chipped,

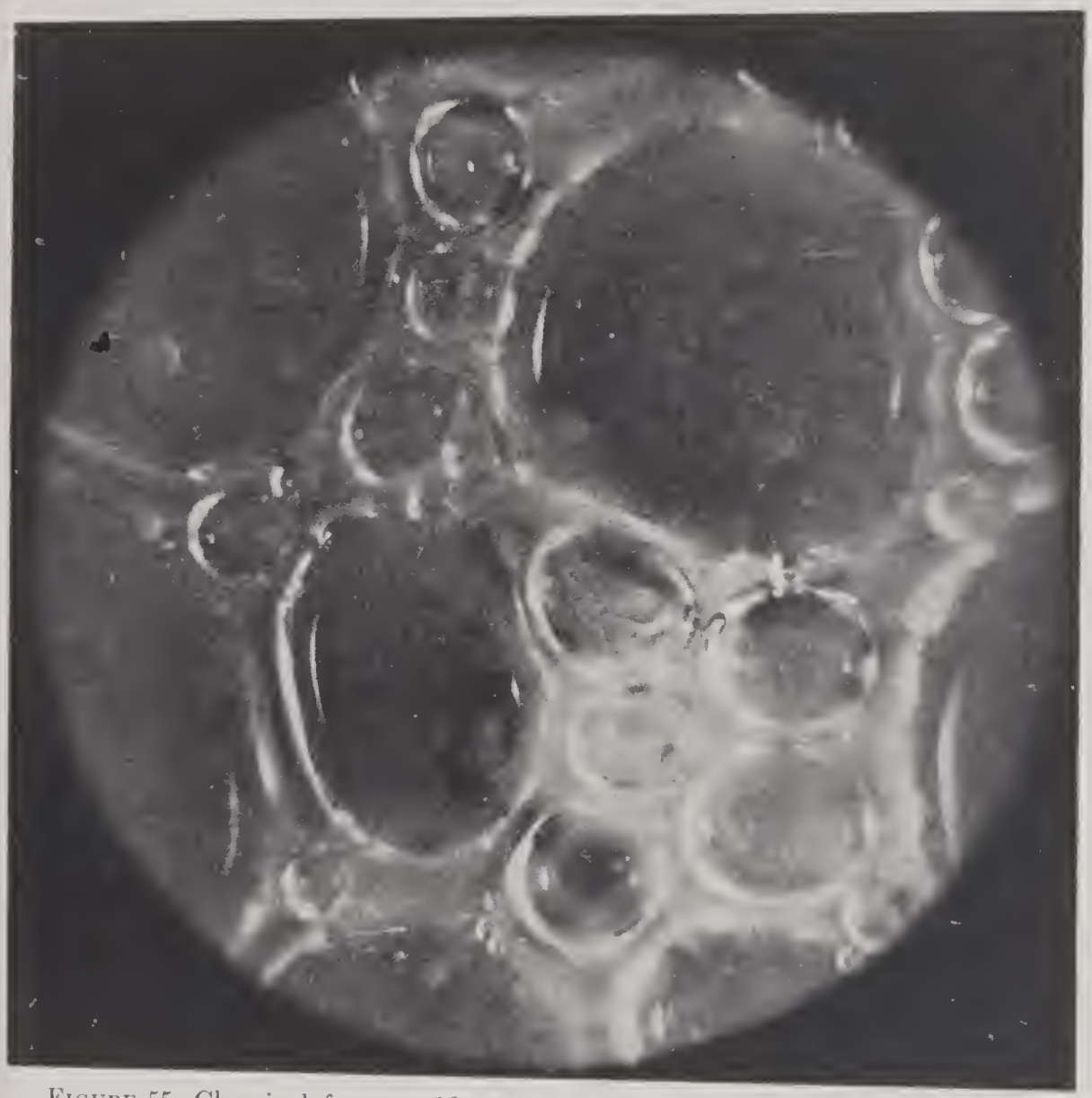


FIGURE 55. Chemical foam: sulfite liquor stabilizer; very fluid foam. Magnification ×30.

caustic soda and water added and digested at 120 psi for ten hours. Sodium sulfite may be used instead of sodium hydroxide. Materials extracted in this manner from roots and wood of spruce, poplar, fir, pine, or licorice are more effective stabilizers than the sodium silicate, glue, or glucose in use at that time. Biddle[39] in 1922 claimed that existing foam compositions were much too expensive and that the waste

products of paper industry could be used to displace the acid and basic constituents in addition to serving as stabilizers. The acid liquor from the sulfite process reacts with that from the soda process to yield a foam. Bicarbonate of soda or limestone, and sulfuric acid, vinegar, or sour whey may be added to hasten the reaction. Blenio[40] in 1924 disclosed a composition having advantages of easy storage, readiness for use, and "positive action" on oils, benzene, naphtha, ether, alcohol, and turpentine. Aluminum sulfate is dissolved in sulfite liquor to increase acidity and viscosity. Sodium bicarbonate is used as it is ordinarily. Esselen[41] in 1925 combined sulfite waste liquor with alkali soaps of rosin. The formula for the composition includes aluminum sulfate and sodium bicarbonate. A Canadian patent in 1926 granted to Ferguson *et al.*[42] recommends the addition of wood flour to improve sulfite liquor.

Section 24. *Fatty Acids.* The first use of fatty acids as foam stabilizers was indicated in a French patent[43] in 1905 in which ammonium acetate was used in the presence of glycerol. Aluminum oleate[44] was mentioned in 1929 by Blenio, and metallic acetates or lactates[45] in 1931 by Fairley. Aluminum, calcium, iron, lead, potassium, magnesium, sodium, or titantium salts are specified in the latter patent. Neutral ferrous acetate, as made from iron scraps and pyroligneous acid, is used in the bicarbonate solution. The first indication of the specific role fatty acids would play in the fire-foam field came with a patent issued to Boyd[46] in 1942. It was noted here that the commercial products, licorice root extracts, saponin, caustic digested peanut shells, in use at that time, produced foams that were readily attacked by alcohols and similar polar solvents. Sodium soaps of tallow fatty acids are caused to react with potassium permanganate in aqueous solution. The reaction products are dried and ground for incorporation into a mixture of aluminum sulfate and sodium bicarbonate to produce a composition for introduction directly into the water line. A British patent[47], somewhat related in function claims the use of a fatty acid soap in conjunction with a regular stabilizer as licorice root or saponin. Alkali resin soaps were patented as stabilizers[48] in France. A patent issued to White[49] in 1946 covers a composition using a stabilizer composed of licorice root extract and zinc, calcium, or magnesium salts of fatty acids having 6 to 18 carbon atoms. Resistance to destruction by alcohols is claimed also for foam composi-

tions containing stabilizers of this description. The alcohol-stable foam compositions disclosed to this date could be used only in the dry form for introduction directly into the water line. Perri[50] in 1952 disclosed compositions which could be stored in solution form and were compatible with the sodium bicarbonate and aluminum sulfate ordinarily used in the portable extinguishers. Ordinarily soluble soaps are salted out in sodium bicarbonate solutions of the concentration required for charging the extinguishers. The resulting gel would

FIGURE 56. Chemical foam: alcohol-stable type used in extinguishing large tank fires.

render operation of the extinguisher ineffectual. Sequestering or dispersing agents as sodium hexametaphosphate, and the tetrasodium salt of ethylene diamine tetraacetic acid were used to keep the bicarbonate-soap solution homogeneous and quick acting for an indefinite period of time. The foam is claimed to be effective in extinguishment of fires involving gasoline; ethyl, methyl, and isopropyl alcohols; esters; ketones; and ethers[51]. In 1941, Goodner *et al.*[52] claimed advantage of greater foam volumes, more rapid foaming action, compatibility with sea water, and insensitiveness to oils for alkali metal salts of alkoxy acetates used to the extent of 15 per cent of the foam composition in place of the 5 per cent usually required for licorice

root, oak bark extract, or butyl naphthalene sulfonate. Alkoxy acetates of formula ROR'COOMe are claimed, where R is an alkyl, aryl, or alkaryl radical, R' is aliphatic divalent radical, and Me is an alkali metal.

Section 25. *Sulfates or Sulfonates.* In 1923 a patent was granted to Kent[53] covering the use of sulfonated mineral oil sludge as a chemical foam stabilizer. Burgess proposed in 1926[54] a procedure for developing this stabilizer to its optimum by controlled aging. A British patent[55] in 1927 covered the sulfonic acid derivatives of aldehyde-phenol condensation products, alkylated napthalene sulfonic acids, and sulfonated higher fatty acids. Chlorinated sulfonic acids were used in conjunction with calcium chloride solutions to obtain reaction at low temperatures displacing the aluminum sulfate used ordinarily for carbon dioxide liberation. A French patent[56] in 1930 covered the use of propyl or butyl naphthalene sulfonic acid and sulfonated castor oil. Thomas *et al.*[57, 58] in 1930 devised procedures for operation of fire extinguishers at −40°F; sodium bicarbonate and halogenated sulfonic acids were used. Also patented were sodium butyl naphthalene sulfonate[59] in 1931, alkyl aryl sulfonic acids[60] as well as sulfates of fatty alcohols[61] in 1933, and water-soluble leuco compounds of triarylmethane dyes containing sulfo groups[62] in 1929. A patent granted to Wright[63] discloses the use, as a foam stabilizer, of sodium octyl sulfite and a buffer material which is present in an amount of about 1 to 1.5 per cent of that of the salt portion of the charge and which may be a phosphate, acetate, or borate of sodium, potassium, or aluminum. In 1939, Holter *et al.*[64] described a procedure for preparation of a stabilizer made by sulfonating a mixture of petroleum hydrocarbon oil and commercial benzol. Benzol used at a minimum of 17 per cent in the mixture gives a more fluid reaction product. The mixture as neutralized with caustic soda is used at 0.1 to 1 per cent concentration based upon total foam solutions. A water-dispersible colloid as gelatin is used in addition to the extent of 0.5 to 2 per cent of the alkali sulfonate mixture. Goodner[65] in 1941 disclosed the use of an alkyl naphthalene sulfonate (Aerosol O S) in conjunction with an alkaline earth metal carbonate for the preparation of the single powder type foam composition (see section 3). The carbonate preferred is a synthetic thought to have the formula $Mg_4(OH)_2(CO_3)_3 \cdot 3H_2O \cdot CaCO_3$. In addition to favoring rapid initiation of reaction, it acts as an

anticaking agent and further it is claimed reacts to increase the heat resistance of the foam. The last claim is unsupported.

Variations in the nature of the acid constituent comprising the foam-forming compositions have already been noted, in particular halogenated sulfonic acids being recommended for use at low temperatures. In 1922 Ferguson *et al.*[66] undertook what they describe as an intensive investigation of the components of the chemical foam charge. In their efforts "to decrease the surface tension of the liquid and increase the surface tension of the foam" they found that glue, saponin, and licorice extract gave the best results. Each, however, has its defects as a stabilizer when tested with aluminum sulfate and sodium bicarbonate. The glue produced a dry foam of low volume, the licorice, large volume and bubble size, and the saponin foam had "much greater surface tension than either." Combination of these stabilizers in the proportions 36.3 glue, 45.4 licorice, and 18.3 saponin in the form of 10 per cent solutions of each resulted in formation of a foam having the most desirable attributes of each stabilizer. The use of aluminum sulfate alone was found deficient in that a continuous film of hydrated aluminum oxide could not be achieved in the foam. Ferric chloride was recommended to produce the desired effect. A British patent[67] likewise covers the use of ferric chloride. Phosphoric acid was disclosed[68] as an alternative for aluminum sulfate as the acid ingredient, and tartaric, citric, and oxalic acids were recommended[69]. The White patent previously described indicates the use of ferric sulfate in single powder chemical foam compositions.

Section 26. *Extracts of Various Plants.* In 1921 Corson[70] claimed that phlobaphenes from waste tanning liquors surpassed glue and soaps as a chemical foam stabilizer; oak bark extract is mentioned in 1925[71] and 1927[72] patents. The latter, issued to Dunlap *et al.*, condemns the fire protection systems based upon storage of solutions of the reactive chemicals in bulk and covers improved process for formulation of powders to be used in single line foam generators. That compositions in use then were subject to deterioration on storage was attributed in part to the high moisture content of the aluminum sulfate. To compensate for the reduced speed of reaction obtained in using dried alum, it was recommended that the particle size be reduced. An inert powder was added to separate the reactants as a further safeguard against deterioration on storage. In 1932 a patent

was granted to Berghausen[73] covering a stabilizer formed from extracts of plants of the family Leguminosae of which alfalfa and clover are best. Extractions may be carried out with acid, neutral, or alkaline liquids. Peanut shells and husks generally were treated by Urquhart[74] in a 10 per cent alkali solution under pressure. The soluble materials extracted were dried and found to be particularly suited to use in foam powders for single-line generators. Tannin-free chestnut and oak bark[75] and vegetable roots in general, beets, turnips[76] and the like were patented.

Section 27. *Miscellaneous.* Schmidt[77] in 1929 worked on a process for improving the storage characteristics of single foam powder. Previous attempts to keep the powder dry by adding hygroscopic materials were unsuccessful. He dried a mixture of aluminum sulfate, sodium bicarbonate, and saponin at 60°C, then mixed it with pumice, ground stone, or sand. There was no appreciable conversion of the bicarbonate at 60°C. Alkaline earth carbonates as additives were patented by Goodner[65] (see section 25) to render the drying ingredients permanently free flowing. Such materials as talc, flour, and China clay[78, 79] can also be used to improve flow characteristics of the powders. In 1933 Beythein[80] recognized that single-powder foam compositions were susceptible to caking on storage and that precaution of heating slowly is a costly process. Instead of three powders his composition contains only bicarbonate of soda and the stabilizer. The carbon dioxide is liberated by using water at a minimum temperature of 80°C. This was recommended particularly for use aboard ship where hot water would be available from the ship's boilers. Further[81], in the manufacture of solid mixtures for producing foam, the commercial air-dry components are oven dried, before mixing, at a temperature about 5° above that at which the mixture is to be stored to reduce the tendency to cake. A German patent[82] in 1933 uses anhydrous sodium carbonate, aluminum sulfate, and foam stabilizer. Anhydrous sodium acid sulfate may replace aluminum sulfate in part.

A German patent[83] proposes the addition of rare earth metal oxides or salts as catalysts plus urea or guanidine to improve adhesion of foams to structural steel.

A series of patents[84] granted to McCracken in 1930 are of interest primarily from the standpoint of foam-producing devices. One apparatus is described for attachment to a water line which in essence splits

the stream into two and provides for a continuous flow of foam powder falling onto the water stream. This idea had not been adopted for hand extinguishers generally. Another device was designed to displace the 40 gal foam engine for the reason that the foam volume maximum for the latter was only 100 gal at that time. The unit provides for mixing two reactive powders in separate hoppers, "creaming" same with water and introducing into water line, meantime charging two other hoppers with powder to achieve continuous foam flow by alternating hopper use. The resulting two solutions are mixed at the site of the fire. In another device provision is made for spraying powder onto sheets of water to obtain rapid solution of the individual components of the foam charge.

In 1943 Urquhart[85] patented another device which allowed for introduction of a single chemical powder containing all of the foam-making ingredients directly into a water line leading to the storage tank to be protected. This type of equipment gained wide acceptance.

Mechanical Foam Stabilizers

Section 28. Although not directly concerned with producing a foam for fire-extinguishing purposes, Jennings'[86] patent in 1922 disclosed principles which had much influence on the development of mechanical foams currently in use. Basically glue, glycerol, and a preservative in aqueous solution were used in conjunction with salts of metals as iron, nickel, or cobalt in their reduced states of valence. Oxidation occurring on mixing with air in the formation of foam supposedly caused deposition of precipitates which further stabilized the foam. This type foam was recommended for use in prevention of evaporation of volatile liquids contained in bulk storage. In the same year improved formulation was disclosed by Jennings; it had the advantages of being more fluid and capable of being re-used. In one case[87] the maximum water content was about 15 per cent and the glycerol content 57 per cent; calcium chloride 20 per cent, ferrous sulfate 1.2 per cent, glue 6 per cent, and soap 0.5 per cent comprised the remainder. The other patent[88] limited the water to 10 per cent and claimed 55 to 70 per cent glucose in addition to glycerol, glue, and ferrous sulfate. These foam patents are of particular interest since they represent one of the first studies of the development of a foaming material which on admixture with air would fulfill certain preconceived specifications and functions. Jennings again in 1924[89, 90] proposed improved formulas containing lesser amounts of water. Proteins

other than the "albuminoid type," as casein, were used to confer "body" to the foam. Cornstarch 5–15 per cent, glycerol 5–30 per cent, alkyl sulfonates, and ferrous sulfate also were included with about 8 per cent water. The resemblance in composition to "marshmallow" is of interest.

The Weidner patent[91] in 1924 is also of importance as a precursor to development of the protein type mechanical foam liquids. It claims procedures for producing soluble surface-active materials from proteins. Neutralization of proteins subjected to limited alkaline hydrolysis by means of mineral acids results in the undesirable formation of an insoluble material. Weidner used fatty acids instead of mineral acids to overcome this deficiency.

Schnabel[92] in 1928 described a system for extinguishing bulk oil fires by use of a mechanical foam containing carbon dioxide. A closed tank was filled with an aqueous solution of a foaming agent as saponin and pressurized with carbon dioxide. On release of the pressure the resulting foam was piped to the fire.

In 1928, Sthamer[93] obtained a patent on a composition which claimed an economic advantage over the use of saponin alone without causing any decrease in foaming properties. It had been the practice to add dextrin or cane sugar as diluents. Sthamer asserted that the foam resulting from such mixtures was inferior. Replacement of these by milk sugar not only reduces cost but improves the lasting qualities of the foam over that of pure saponin, Further, dextrin or cane sugar could be used only to the extent of 30 to 40 per cent, whereas a 83:17 mixture of milk sugar and saponin produced a foam which is as good as that of pure saponin. The ratio recommended for fire-extinguishing purposes was 75 to 25. Dachlauer *et al.* in 1929[94] produced a frothing agent from halogenated carbonyl compounds and phenols. A typical reaction is:

$$CH_2ClCHClOC_2H_5 + 3C_6H_5OH \rightarrow$$

$$HOC_6H_4CH_2CH(C_6H_4OH)_2 + 2HCl + C_2H_5OH$$

Treichel[95] in 1934 demonstrated the use of the licorice root extracts (see section 21) in the preparation of an air foam liquid. Claims are made for economy in production and reduced bulk of the liquid in

addition to foam of improved quality. The licorice root extract was mixed with hydroxides of calcium, barium, or strontium in ratio of 3:1. Regulation of the consistency of the mixture, a factor of importance in cases where it must be proportioned mechanically into water, was obtained by altering the aforementioned ratio. A 4 per cent mixture with water was aerated into foam, then pumped by a three stage gear pump into the water stream.

Gross *et al.*[96] in 1937 claimed stable and efficient fire foams by adding materials of formula

$$R_1(OCH_2CH_2)_nOR_2$$

where R_1 = H or alkyl; R_2 = H or alkyl, aryl, alkaryl; and $n > 3$ to solutions having high wetting and foaming powers as sulfonated vegetable oils or alkyl aryl sulfonates. Further added were "cellosolves," urea, thiourea, alkylated cellulose, or degraded albumoses.

Hood[97] in 1935 patented a method of producing fire-foam which involved the use of a mixture of equal parts of sulfite cellulose liquor, chlorides of calcium and magnesium, and glycerine foots. The latter are obtained as a residue in the commercial purification of glycerol from a soap manufacture by-product. The cellulose liquor-glycerine foots mixture can be prepared separately for addition to the salt solution when and where needed. This is one of the first attempts to achieve a preparation that can be used below 32°F. The recommended method for use was to provide for dispersal of air into the container thereby making foam which is forced out of discharge outlets. A heavy foam which lasts for days is claimed.

In 1939, Timpson[98] disclosed the use of potassium or ammonium soaps made from nondrying oils, such as coconut oil, having an iodine number below 25. The type of foam produced was dependent upon the hardness of the water with which the foam liquid was used.

High molecular weight quaternary ammonium, phosphonium, and sulfonium compounds were proposed by Bertsch[99] in 1938 for production of foams capable of withstanding the destructive effects of alcohols. Lauryl pyridinium sulfate is cited as a leading example. Quinoline and isoquinoline may be substituted for pyridine and straight-chain hydrocarbons containing not less than 8 carbon atoms for the lauryl. Numerous examples are given which cover for the most part all related types. It is claimed that a dense foam is formed which is not destroyed on contacting hot steel surfaces.

In 1939 Sthamer[100] contended that in spite of their advantages from

the standpoint of application, existing mechanical foams were deficient in covering quality (see section 17) and lacked adhesion as compared to chemical foam. His patent covers the use of solubilized

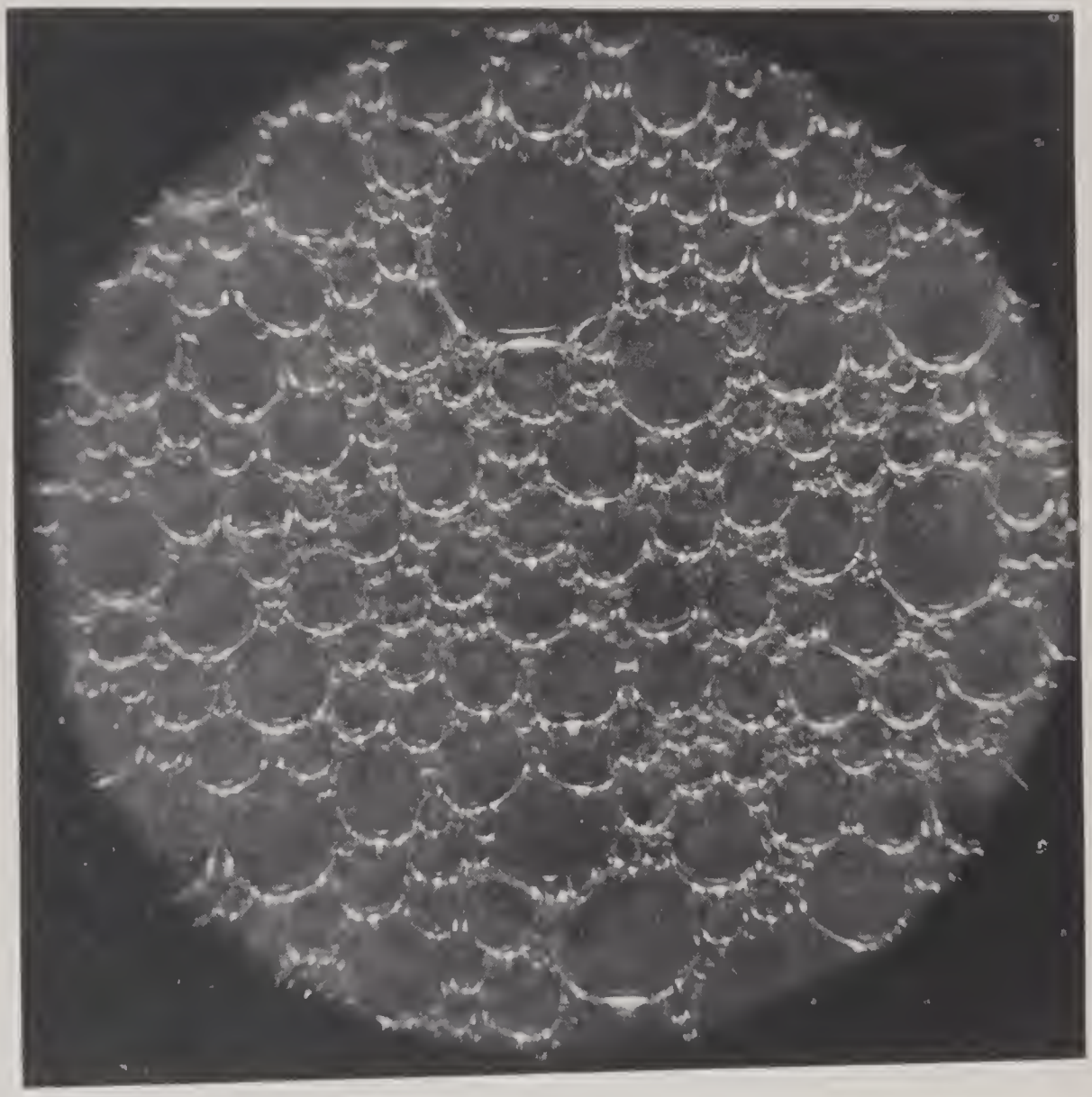


FIGURE 57. Mechanical foam: protein type; 8 per cent stabilizer. Magnification ×30.

animal or vegetable proteins in conjunction with salts of metals of variable valency and states that this differs from the Jennings patent in that the latter used colloidal glue and not truly soluble dissociated proteins. In the case where ferrous iron is used it is postulated that oxidation occurs producing a ferric-protein precipitate which serves as a solid skeleton for the foam.

The use of protein materials was also disclosed in 1939[101] by Daimler *et al.* This was recommended, however, in conjunction with synthetic wetting agents, which acted as primary foam formers while the pro-

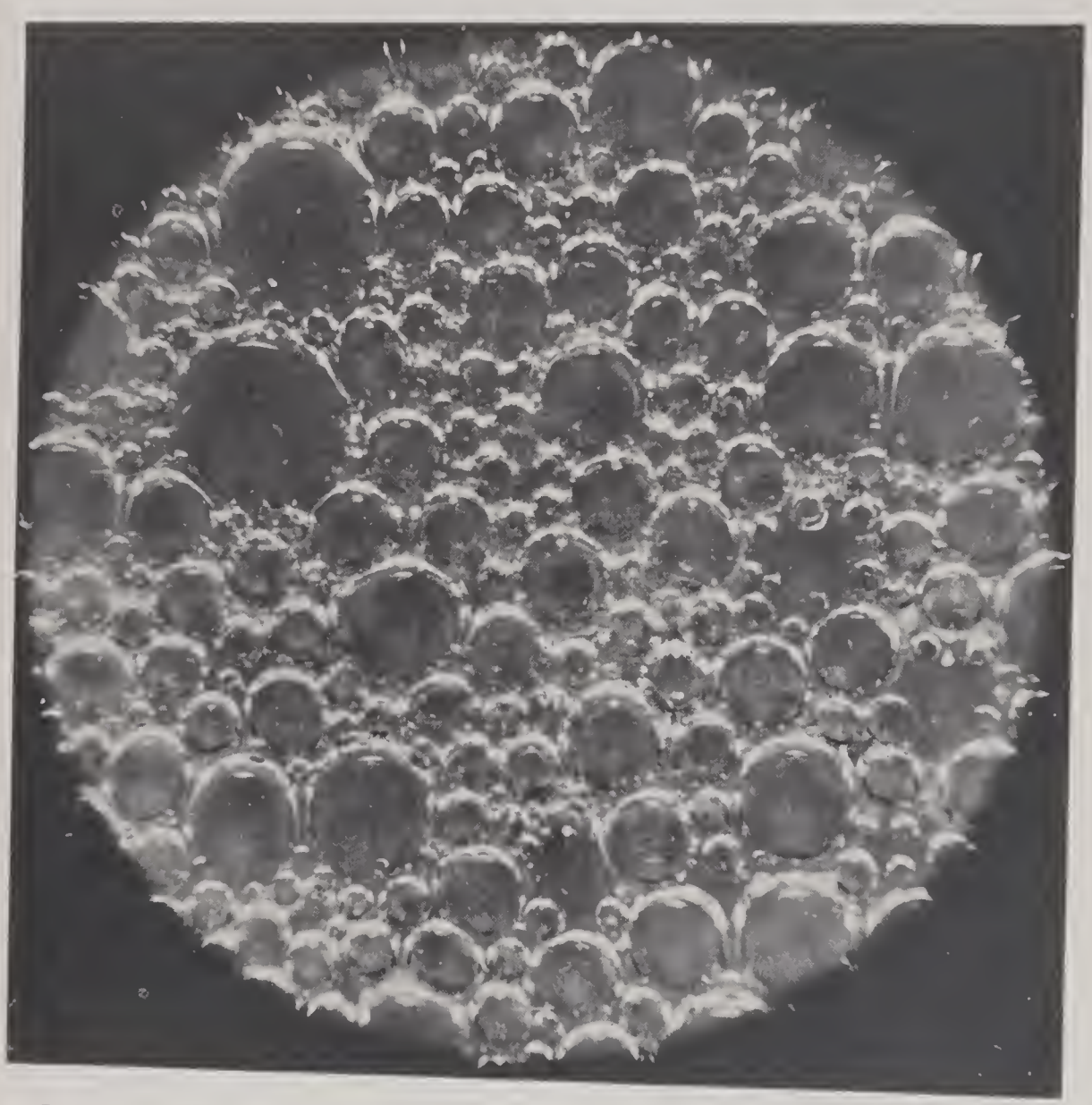


FIGURE 58. Mechanical foam: protein type; 4 per cent stabilizer. Magnification ×30.

teins acted as stabilizers. The art of protein degradation for production of a foam of satisfactory volume had not been achieved. The composition claimed a minimum of 13 per cent wetting agent, 20 per cent of albumen degradation product, and 50 to 60 per cent of a mixture of water and a hydrophilic solvent. The wetting agents are from the classes such as alkylaryl sulfonic acid (salts) or sulfonated fatty

alcohols. No protein other than albumen is mentioned. Alcohols, glycols, and esters soluble in water compose the group of hydrophilic materials.

Daimler *et al.*[102] proposed in the year 1939 the use of highly concentrated synthetic wetting agent solutions. The increased solubility of the wetting agent, such as sodium butyl naphthalene sulfonate, was effected by the use of co-solvents themselves readily miscible with water. Alcohols, glycols, esters, or combinations of such served in this capacity. It was claimed that foam formed from this concentrate possessed stability of a much greater degree than that made from aqueous solutions of wetting agents. The claims are made for a process for making fire-extinguishing foam.

Timpson[103] in 1940 recognized the necessity of ready solubility and ease of dispersability as important properties of a mechanical foam liquid that would ease foam formation in fire-fighting practice. Soluble phosphated salts of fatty alcohols or fatty acid glycerides in the form of a 12 per cent aqueous solution comprised the foam liquid concentrate. When this concentrate was used with 16 parts of water the foam was particularly resistant to hot vapors. The best agents are said to be the phosphated inorganic sulfonates of fatty alcohols such as lauryl, stearyl, or their mixtures.

In 1940 Timpson[104] patented a method of making fire-extinguishing foam based upon the use of an aqueous solution of alkanol amine soaps. The best foam for extinguishing oil fires is obtained by using saturated fatty acids having between 5 and 20 carbon atoms. For commercial preparations coconut or palm kernel oils were considered particularly satisfactory. Equimolecular quantities of the alkanol amine may be used; however, slight excesses are recommended to provide for free flowing at low temperatures. Glycols may also be added for antifreeze performance. This patent which covers both the product and method for making the foam claims that up to 1,400 gal of foam are produced from 1 gal of foam liquid. A 3 per cent solution was recommended for use commercially.

Freidrich[105] in 1940 patented foam-forming compounds having higher stability and resistance to heat. He recommended these for use on fires involving alcohols and aromatic hydrocarbons in addition to regular petroleum products. The compounded mixture according to this invention consists of solubilized proteins in aqueous solution containing aluminum salts. Aluminum acetate formed *in situ*, aluminum lactate, or aluminates may be used. The pro-

tein (keratin is mentioned) is solubilized by heating in a suspension of lime. Aluminum salts generally confer increased viscosity and stability to protein foams; however, in practice they have not been found effective in rendering the foam bubble more resistant to the destructive action of alcohols.

In 1941 Daimler[106] stated that the mechanical foams made thus far cannot be used for extinguishing fires involving alcohol, acetone, and other low molecular weight polar solvents. Recommended as suitable is a mixture comprised of (a) complex ammonia salts of copper or zinc, (b) salts of fatty acids having 7 to 11 carbon atoms, and (c) protective colloids as gelatin, glue, or degraded albumen, and water-soluble derivatives of pectin, algin, lignin, sulfolignin, humic acid, sugars, and molasses. The protective colloids are mixed with the fatty acids and an excess of ammonia; then an aqueous solution of the metal salt is added. The special alcohol resistance of this foam is not achieved in the instant of foam formation. At least one-half min. is required for the foam to develop its alcohol resistance and it is recommended that the foam be allowed to flow through a pipe to ripen.

In 1942 Urquhart[107] obtained a patent on a process for producing a stable fire-extinguishing foam for petroleum fires from soybean protein hydrolysate. It is claimed to have achieved cohesive and adhesive properties not obtainable by other means, the foam blanket being unusually rigid. Various means of hydrolysis are given for preparation of stabilizers to be used in chemical or mechanical foam. The hydrolytic treatments described involve the use of sodium hydroxide, sulfuric acid, potassium permanganate, nitrous acid, and oleic acid in aqueous medium.

Ratzer[108] in 1943 proposed a scheme for the hydrolysis of protein materials for manufacture of mechanical foam liquids. Animal proteins, principally keratins, albumens, globulins derived from horns, hoofs, hair, feathers, blood, and vegetable proteins from soybean meal, pea flour and maize meal were mentioned. The hydrolysis is carried out preferably with lime to such an extent that 25 to 50 per cent of the nitrogen present in the water-soluble products exists in the form of peptones. A one per cent solution of a neutral 50 per cent concentrate of these products yields an expansion of six in suitable field apparatus. The addition of iron salts is not necessary, according to this patent, since the hydrolysis products are sufficiently stable.

In 1944 Ratzer[109] covered substantially the same chemistry as indicated in his previous patent[108]. The claims, however, are directed

at covering methods "of producing fire-extinguishing foam by the manner of incorporation of a gas into a stream of water having dissolved therein hydrolysis products of protein" obtained as described above.

Bagley *et al.*[110] in 1944 claim that all foams to date have been unsatisfactory from foam volume and stability standpoints. Their invention is productive of a foam which is "thick and copious and long lasting." The hydrolysis products of proteins are used. Glue is hydrolyzed by heating in a 5 to 10 per cent solution of sodium nitrate. The resulting solution can be concentrated without the formation of a precipitate. The nitrate improves the performance in cold weather and in sea water, and reduces corrosion and mold or bacterial growth. Synthetic organic wetting agents as alkylaryl sulfonates or sulfonated alcohol are added to provide an abundance of foam, the protein acting as stabilizer.

Tresise *et al.* [111] indicated in 1945 that the most successful type of mechanical foam liquid up to that time was that due to Ratzer[108]. The main objection was that sediment formation was likely when the hydrolyzate containing calcium ions was neutralized with sulfuric acid. This invention proposes to remedy the situation by using hydrochloric in place of sulfuric acid. Advantages are claimed in the maintenance of the final pH between 6.5 and 7.0 when iron salts are added; below this range the foam is supposedly less stable to gasoline vapors.

In 1946 Levin[112] claimed that processes patented thus far for the hydrolysis of protein materials were of limited utility. The treatment of soybean meal[107] with caustic soda or acid resulted in a weak foam that had to be stabilized by addition of inorganic salts; the lime treatment[108] to obtain 50 to 60 per cent peptone was too degenerative of the protein to permit stable foam formation. Gum formation on hydrolyzing with lime also led to difficulty in handling during processing. Cottonseed and peanut cake were found to be the only ones suitable for the formation of the desired proteoses, according to this invention, by lime hydrolysis. It is important to degrade to the extent that not more than 20 per cent peptones are formed.

In 1946 Urquhart[113] proposed the addition of glycols and glycol ethers to the soybean composition described in the earlier patent for the purpose of increasing foam volume and stability and obtaining liquids more readily dispersible in water and more fluid at lower temperatures. Complete details are given for the lime hydrolysis of

the soybean protein and its subsequent acid treatment. The glycols were added to the extent of 15 per cent by volume to the concentrated hydrolysate. The 25 to 30 per cent concentrate was recommended for use in a 3 to 9 per cent mixture with water.

Keil *et al.*[114] in 1947 found that a solution of a completely hydrolyzed protein used in conjunction with metallic salts gives a foam good in all respects but flow characteristics. A mild hydrolysis does not provide as satisfactory a foam and the addition of metal salts renders it too rigid. The invention revealed is concerned with a mild hydrolysis and subsequent removal of the "foam inhibitive" portion of the protein hydrolyzate. Histones, protamines, globins, globulins, albumens, keratins, prolamines, gluten, casein, and mucin as found in blood, horn and hoof meal, hide, and hair are most suitable. Enzyme hydrolysis also is mentioned, pancreatin or papain being used at 40°C. and pH of 5 to 8.

It is postulated that the high molecular weight fractions are removed by pH adjustment to 4.5–4.8. This apparently applies to blood but not to proteins in general in view of work of Perri and Hazel[115].

In 1949 Perri[116] claimed that the utility of mechanical foam liquids is greatly increased if means are established to produce a foam liquid of controlled viscosity. This invention produced a liquid the viscosity of which is inappreciably affected by the temperature. The advantages are obvious since at this time most devices depended upon proportioning of liquid through standard orifices. Primarily urea addition served to render the viscosity substantially independent of the temperature. Further, the urea tends to render soluble inorganic salts, ferric iron in particular, and to keep such in solution permanently. The composition contained hydrolyzed soybean protein, glycol ethers, alcohols, ferric chloride, and urea.

In 1949 Ratzer[117] obtained a patent on a composition so designed as to prevent the formation of a precipitate or scum on aging of a protein hydrolyzate concentrate containing added iron salts. He attributed scum formation to a reaction akin to that which occurs between iron and protein when the foam is made. Addition of the iron salts is made in excess after neutralization of the alkaline hydrolysate and the precipitate is allowed to form during the concentration of the hydrolyzate from which it is readily filtered. Horn and hoof meal is cited in the example.

Busse *et al.*[118] claim a mixture of synthetic surface-active agents capable of producing foam of high heat stability and slow drainage.

The foaming agents are of the type N-acyl-N-alkyl taurines and their alkali salts, where the acyl and alkyl radicals have more than 7 carbon atoms. The foam stabilizer is a copolymer of vinyl alkyl ether and maleic anhydride. A concentrate may be prepared containing 20 per cent of the two reagents and used at 1 per cent concentration. In the same year, Busse *et al.*[119] stated that protein foams are not sufficiently stable toward heat and as a consequence great quantities must be used in extinguishing fires. Carboxylmethyl cellulose was used as the foam stabilizer in the form of its sodium, potassium, or ammonium salts and a wetting agent as sodium lauryl sulfate was the foam producer. A foam formed from an aqueous solution containing 0.5 per cent of the former and 1 per cent of the latter was claimed to excel in fluidity (see section 13), covering quality (see section 17), imperviousness to vapors, and heat resistance. The fire test data on the effectiveness of this composition appears to present glaring inconsistencies when viewed in the light of present-day practices. A gasoline fire covering an area of 475 sq ft and involving 100 gal of gasoline (approximately $\frac{1}{3}$-in. depth) was extinguished when foam was applied at the rate of 200 gpm of solution through a foam nozzle after a 10-sec preburn. When a commercial protein foam was applied to a second fire under the same conditions, the fire was not extinguished, it was claimed. The rate of solution application calculates to be 42.1 gpm/100 sq ft of burning area. The fire test described in the U. S. Government Specifications JAN-C-266 for protein-type foam liquids specifies that the rate of application be 6 gpm for a 100-sq-ft gasoline fire. The protein materials meeting these specifications encounter no difficulty in extinguishing the fire in a rapid manner in spite of the fact that the rate of application is about one-seventh of that described in the Busse patent.

Swift[120] in 1950 claimed that the use of sulfuric acid in the neutralization of protein hydrolyzates gave rise to many complications. In addition to the hazards encountered in its handling, sulfuric acid causes precipitation of metaprotein which is difficult to redissolve. Water-soluble salts which react with calcium ions were used to neutralize a lime hydrolyzate of zein. The bicarbonate is preferred since no extraneous ions remain in the solution, although oxalate, sulfate, or tartrate may be used. Metal salts containing ferrous iron, freezing point depressants, and preservatives were added.

Keil *et al.*[121] in 1950 maintained that the chemical hydrolysis of

proteins usually results in the formation of certain soluble inorganic salts which are a hindrance to the addition of stabilizing salts as ferrous sulfate, etc. Enzyme hydrolysis of the proteins renders iron introduction easy. The keratinaceous materials such as hoof, horn, and hair are pretreated to remove the anti-enzyme factors and to

FIGURE 59. Mechanical foam: standard fire test (JAN-C-266); preburn period.

remove or fix the sulfides present so as not to interfere with the iron addition. The keratin is heated in alkali to accomplish anti-enzyme removal and treated with organic acid to facilitate iron introduction.

Anionic or nonionic surface-active agents in combination with karaya gum were patented[122] in 1950. The sodium salts of N-hexyl and N-octyltaurine and the ammonium salt of tri-isobutylsulfotricarballylate were used at concentrations of 0.25 to 5 per cent to produce a "self-sealing, gas impermeable" foam.

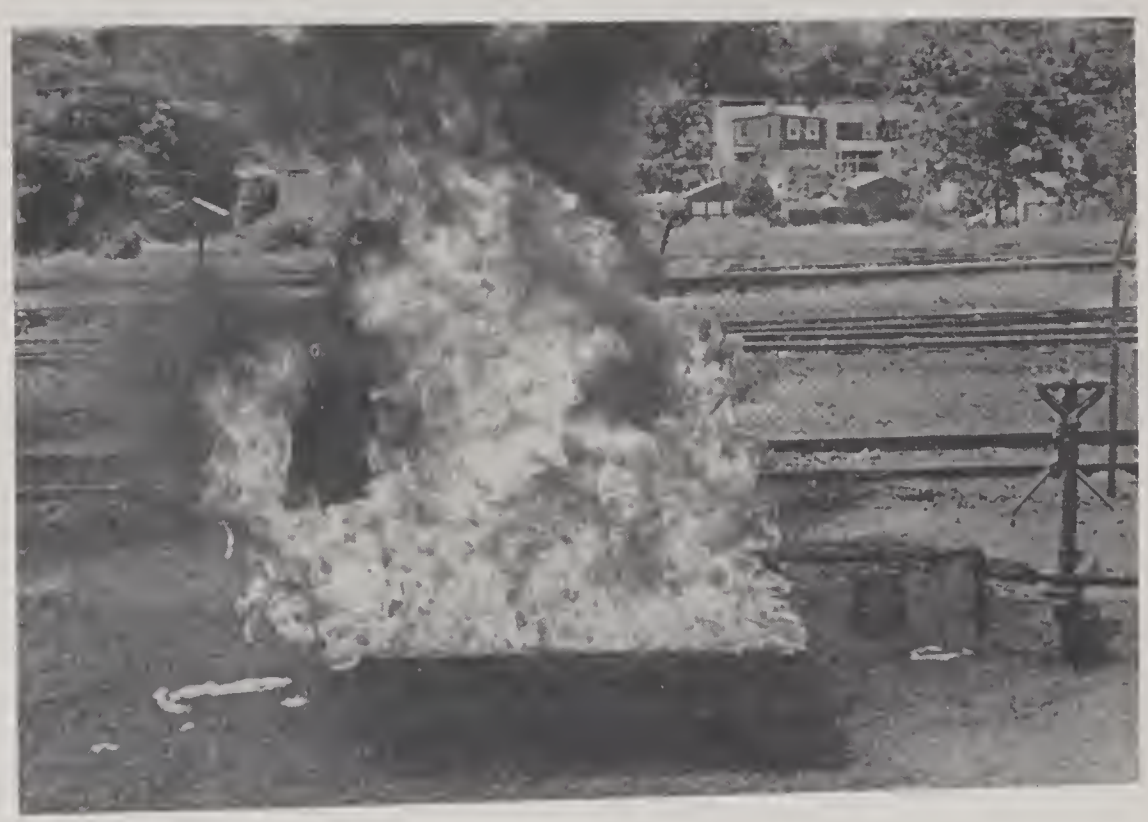
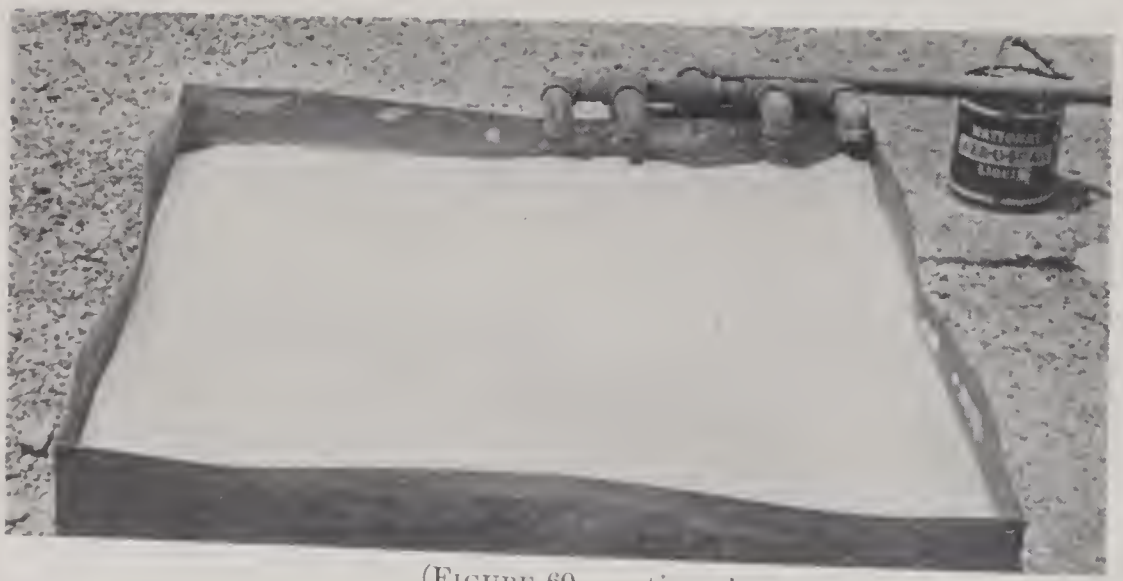


FIGURE 60. Control of gasoline fire by application of foam. (A) Tank before fire is started; application of foam at the rate of 2 gpm per sq ft; (B) free-burning gasoline fire; (C) foam application started; (D) foam coverage obtained; (E) foam blanket—control obtained.

(C)

(D)



(E)

(FIGURE 60, continued)

Section 29. *Foreign Patents.* The material contained in the patents reviewed in this section has, for the most part, already been covered.

Proteins. The use of wetting agents in conjunction with proteins was shown in two British patents in 1937. Glue hydrolyzed with nitric acid[123] was used in one case and degraded albumen in the other[124].

The use of ferrous sulfate in degraded protein solutions is shown in a British patent[125] in 1937.

Moilliet and Todd[123] in 1937 proposed use of a mixture of nitric acid treated glue and a wetting agent of high foaming power. The advantage claimed is that improved viscosity characteristics are achieved over ordinary glue. Further, soluble nitrates are formed by neutralization with caustic soda causing a freezing point reduction to zero. Ethyl alcohol or the like is added in addition to wetting agents as isobutylnaphthalene sulfonates.

Later, hoof and horn meal was hydrolyzed with caustic soda and used in conjunction with black sulfite liquor[126].

In Germany, improved results were claimed for use of potassium hydroxide as the hydrolyzing agent for albumens[127].

Biological degradation of proteins using enzymes or bacteria was mentioned[128] as a practical means for producing a foaming hydrolyzate in 1939.

Ratzer[129] in 1940 suggested a means for controlling the hydrolysis of proteins, scleroproteins in particular. He considered the optimum degree of hydrolysis was obtained when a 1 per cent solution of the soluble products gave 6 to 16 volumes of foam for each volume of solution and when a neutral 50 per cent solution of the soluble products yielded no precipitate on addition of 10 per cent of a concentrated ferrous sulfate solution.

A British patent[130] is based upon the addition of saponin to hydrolyzed blood.

In 1941 Migray[131] used amino acids "that are not carbonized by heat and cannot be distilled without decomposition." To aqueous solutions of various salts, such as magnesium or sodium chloride, saturated at 0°C. he added polyhydric alcohols, ketones or their derivatives, molasses, lignosulfonic acid, and amino acids. The advantages claimed are mostly economic since the amino acids may be obtained from leather factory wastes.

A German patent[132] in 1942 showed the addition of small amounts of soluble aluminum salts as capable of increasing the fire resistance of foams from protein hydrolysates.

Tresise *et al.*[133] claimed advantages in 1944 for the use of hydrochloric acid in neutralizing a lime-degraded protein solution.

In 1943 Mattin *et al.*[134] patented the use of fish scale proteins as a raw material to be hydrolyzed chemically or enzymatically for the manufacture of a foaming hydrolyzate. A wetting agent and a common solvent are preferably added to improve the foam volume and quality. A typical mixture contained about 3,600 lb of a 35 per cent protein concentrate, 400 lb of monobutyl ether of hydroxy diphenyl, 250 lb of butyl "Cellosolve," 1,700 lb of water, and 25 lb of cresylic acid.

Sulfonates. A Canadian patent[135] in 1946 discloses the combination of a sulfonated foaming agent and a water-soluble salt of an acid containing at least three carbonyl groups as triethanolamine citrate which is cited.

A Swiss patent[136] in 1949 indicated higher alkyl sulfates of formula $RR'CHSO_4X$ as productive of suitable foam for fire-extinguishing purposes.

A British patent[137] commented in 1946 that ordinary soaps and even most sulfonates do not work effectively with sea water. The addition of polycarboxylic acids to sulfonates was found to render the mixture effective when used with sea water. Aconitic or tricarballylic acids were found to be most effective as calcium dispersing agents. Mixtures of fatty acids were used to take advantage of the good foaming power of the shorter chains and the foam-stabilizing ability of the longer. Although the longer molecules are the less soluble in sea water they are readily solubilized by the more soluble compound when comprising from 12 to 50 per cent of the mixture.

Miscellaneous. A variety of complex organic preparations are recorded in the patent literature.

A French patent[138] proposed the addition of a solvent of the formula $R'OCH_2(CH_2OCH_2)_nCH_2OR$ to a wetting agent solution. Diethyleneglycol monoethyl ether was added to the N- methyltauride of oleic acid in a typical case.

A German patent[139] in 1937 presented aqueous solutions of salts of high molecular weight nitrogen bases, typical of which is carbododecyloxymethyl trimethyl ammonium chloride. A French patent[140] is similar.

A French patent[141] in 1935 described water-soluble salts of aliphatic amines containing an aliphatic chain of more than ten carbon atoms

attached to a nitrogen atom. Benzyl dimethyl dodecyl ammonium chloride is typical.

Another French patent[142] in the same year covered ammonium, phosphonium, and sulfonium compounds of high molecular weight. Lauryl pyridinium sulfate is cited.

References

1. Laurent, *Imp. Russian Tech. Inst., Chem. Sect.* (1904).
2. Simonis, H. S., *Inst. Fire Engrs.*, **47,** (1933).
3. Wagener, British Patent 272,993; also Muller, British Patent 528,369.
4. Schroeder and Van Deurs, British Patent 306,550; Ellehammer, British Patent 347,048; Komet Kompagnie, British Patent 403,291.
5. U. S. Joint Army-Navy Specification JAN-C-266.
6. U. S. Joint Army-Navy Specification JAN-C-267 (Dec. 1945).
7. Underwriters' Laboratories Report, "Standard for 2½ Gallon Foam Extinguisher," Chicago, Ill.
8. Underwriters' Laboratories Report No. EX1798 (1951).
9. Perri, J. M., Unpublished report.
10. Michaelis and Rona, *Biochem. Z.*, **15,** 196 (1909).
11. Perri, J. M., and Hazel, J. F., Foam Symposium, Am. Chem. Soc. Meeting, Chicago, Sept. 1950.
12. Perri, J. M. (to National Foam System, Inc.), U. S. Patent 2,594,985 (1952).
13. Perri, J. M., and Dollman, D. Y., U. S. Patent Application (1951); Perri, J. M., and Sloviter, Benj., U. S. Patent Application (1952).
14. Underwriters' Laboratories, "Report on National '99' Foam Powder," Report No. EX1112 (Nov. 1940).
15. "Standards for Foam Extinguishing Systems," p. 28, No. 11, 1951, N.F.P.A., Boston, Mass.
16. Underwriters' Laboratories Report No. EX1677 (1950).
17. Underwriters' Laboratories Report No. EX1798 (1951).
18. Friedrich, K., Foam Conference Report; Apolda (June 2, 1943).
19. Tuve, R. L., and Peterson, H. B., "A Study of Some Mechanical Foams, etc.," Naval Research Lab., Rept. No. 3725 (Aug. 23, 1950).
20. Clark, N. O., Special Report No. 6, D.S.I.R., H. M. Stationery Office, London, 1947.
21. "Foam Manual," National Foam System, Inc., West Chester, Pa. (1950).
22. Amsel, O., *Oel u. Kohle*, **38,** 291 (1942).
23. Grove, C. S., Jr., *et al., Ind. Eng. Chem.*, **43,** 1120 (1951).
24. Brunswig, *Feuerschutz*, **2,** 30 (1942).
25. Fry, J. F., and French, R. J., *J. Appl. Chem.*, **1,** 429 (1951).
26. Fry, J. F., and French, R. J., *J. Appl. Chem.*, **1,** 425 (1951); French, R. J., *J. Appl. Chem.* **2,** 60 (1952).
27. Erwin, O. R., and J. B., U. S. Patent 1,247,803 (1917).
28. Van Leuven, L. B., and H. C. (to Vacuum Oil Co.), U. S. Patent 1,507,943 (1924).

29. Bartels, E. (to Patentirtes Schaumloschverfahren Perfect Gesellschaft), U. S. Patent 1,115,887 (1914).
30. Money, G. J., British Patent 170,390 (1920).
31. Phillips, W. B., British Patent 214,075 (1924).
32. Gregory, G. A. (to Minimax, Ltd.), British Patent 227,936 (1923).
33. Thomas, C. A., and Hochwalt, C. A. (to Fyr-Fyter Co.), U. S. Patent 1,973,734 (1934).
34. White, C. B. (to American-La France Foamite Corp.), U. S. Patent 2,355,935 (1944).
35. Rheem, W. S., Chappell, M. L., and Black, J. C., U. S. Patent 984,853 (1911).
36. Crosby, P. A., and Matheros, R. R. (to Roxana Petroleum Co.), U. S. Patent 1,375,779 (1921).
37. Urquhart, G. G. (to National Foam System, Inc.), U. S. Patent 2,269,958 (1942).
38. Walker, W. W. (to MacAndrews and Forbes), U. S. Patent 1,219,509 (1917).
39. Biddle, A. (to United Products Corp. of America), U. S. Patent 1,428,207 (1922).
40. Blenio, G., U. S. Patent 1,489,692 (1924).
41. Esselen, G. J., Jr. (to Badger Fire Extinguisher Co.), U. S. Patent 1,558,599 (1925).
42. Ferguson, G. E., and Timpson, L. G. M. (to Pyrene Mfg. Corp.), Canadian Patent 262,213 (1926).
43. Antignit Gesellschafft, Ltd., French Patent 354,445 (1905).
44. Blenio, G., U. S. Patent 1,707,597 (1929).
45. Fairley, T. J. (to Hunter, W. J. and M. P.), U. S. Patent 1,832,109 (1931).
46. Boyd, F. L. (to National Foam System, Inc.), U. S. Patent 2,269,426 (1942).
47. Blakeborough, R. A., and Garratt, W. R., British Patent 369,012 (1931).
48. Minimax (Soc. Anon.), French Patent 764,138 (1934).
49. White, C. B. (to American-La France Foamite Corp.), U. S. Patent 2,405,538 (1946).
50. Perri, J. M. (to National Foam System, Inc.), U. S. Patent 2,594,985, (1952).
51. Underwriters' Laboratories Report No. 1677 (1950).
52. Goodner, E. F., and Dittus, F. W. (to Standard Oil of Calif.), U. S. Patent 2,250,182 (1941).
53. Kent, G., U. S. Patent 1,441,728 (1923).
54. Burgess, L., U. S. Patent 1,599,006 (1926).
55. Chapman, E. (British Dyestuffs Corp., Ltd.), British Patent 289,630 (1927).
56. I. G. Farbenind., A.-G., French Patent 665,017 (1930).
57. Thomas, C. A., and Hochwalt, C. A., U. S. Patent 1,777,338 (1930).
58. Thomas, C. A., and Hochwalt, C. A., U. S. Patent 1,777,339 (1930).
59. I. G. Farbenind., A.-G., German Patent 528,774 (1927).
60. Daimler, K. (to General Aniline Works), U. S. Patent 1,914,406 (1933).
61. H. Th. Böhme, A.-G., German Patent 554,520 (1929).

62. Krzikalla, H., and Guthke, W. F. (to I. G. Farbenind., A.-G.), German Patent 539,150 (1929).
63. Wright, V. W. (to Fyr-Fyter Corp.), U. S. Patent 2,289,688 (1942).
64. Holter, C. B., and Stewart, E. L. (to The Texas Co.), U. S. Patent 2,166,008 (1939).
65. Goodner, E. F. (to Standard Oil Co.), U. S. Patent 2,258,587 (1941).
66. Ferguson, G. E., and Eckelmann, L. E. (to Pyrene Mfg. Corp.), U. S. Patent 1,421,436 (1922).
67. The Pyrene Co., Ltd., British Patent 206,045 (1924).
68. Austin, R. W., U. S. Patent 1,815,963 (1931).
69. Burmeister, H. (to Pyrene-Minimax Corp.), U. S. Patent 1,732,218 (1929).
70. Corson, B. I., U. S. Patent 1,401,240 (1921).
71. U. S. Patent 1,572,403 (1925).
72. Dunlap, F. L., and Ewer, N. T., U. S. Patent 1,624,398 (1927).
73. Berghausen, A. (to E. Berghausen Chemical Co.), U. S. Patent 1,848,042 (1932).
74. Urquhart and Jones (to American Fomon Co.), U. S. Patent 1,922,510 (1933).
75. Ewer, N. T. (to Amdyco Corp.), U. S. Patent 1,562,878 (1926).
76. May, J. (to M. and P. Colloid Stabilizers, Ltd.), British Patent 560,354 (1944).
77. Schmidt, K. (to Pyrene-Minimax Corp.), U. S. Patent 1,739,094 (1929).
78. Amdyco Corp., French Patent 632,731 (1927).
79. Dunlap, F. L., and Ewer, N. T. (to Amdyco Corp.), U. S. Patent 1,624,398 (1927).
80. Beythein, R. (to Pyrene-Minimax Corp.), U. S. Patent 1,908,398 (1933).
81. Excelsior Feuerlöschgeräte, A.-G., German Patent 578,103 (1933).
82. Neuville, F., German Patent 583,231 (1933).
83. Fuchs, E., German Patent 485,400 (1925).
84. McCracken, J. A., U. S. Patents 1,781,292-3-4-5 (1930).
85. Urquhart, G. G., U. S. Patent 1,954,154 (1934).
86. Jennings, J. M. (to Standard Oil Development Co.), U. S. Patent 1,423,719 (1922).
87. Jennings, J. M. (to Standard Oil Development Co.), U. S. Patent 1,423,720 (1922).
88. Jennings, J. M. (to Standard Oil Development Co.), U. S. Patent 1,423,721 (1922).
89. Jennings, J. M. (to Standard Oil Development Co.), U. S. Patent 1,443,538 (1924).
90. Jennings, J. M. (to Standard Oil Development Co.), U. S. Patent 1,495,308 (1924).
91. Weidner, E., U. S. Patent 1,489,181 (1924).
92. Sehnabel, R. (to Minimax, A.-G.), U. S. Patent 1,669,213 (1928).
93. Sthamer, E., U. S. Patent 1,696,507 (1928).
94. Daehlauer, K., and Thomsen, C. (to I. G. Farbenind., A.-G.), U. S. Patent 1,732,503 (1929).
95. Treichel, J. B. (to MacAndrews and Forbes), U. S. Patent 1,971,997 (1934).
96. Gross et al. (to I. G. Farbenind., A.-G.), U. S. Patent 2,088,085 (1937).

97. Hood, O. E. (to Myrtle Hood), U. S. Patent 2,122,883 (1938).
98. Timpson, L. G. M. (to Pyrene-Minimax Corp.), U. S. Patent 2,135,365 (1939).
99. Bertsch, H. (to Böhme Fettchemie-Gesellschaft), U. S. Patent 2,136,963 (1938).
100. Sthamer, E. (to Fabrike Chemischer Prop.), U. S. Patent 2,151,398 (1939).
101. Daimler, K., Paquin, M., and Reidelsberger, W. (to I. G. Farbenind., A.-G.), U. S. Patent 2,154,231 (1939).
102. Daimler, K., Paquin, M., and Reidelsberger, W. (to I. G. Farbenind., A.-G.), U. S. Patent 2,165,997 (1939).
103. Timpson, L. G. M. (to Pyrene-Minimax Corp.), U. S. Patent 2,193,541 (1940).
104. Timpson, L. G. M. (to Pyrene-Minimax Corp.), U. S. Patent 2,196,042 (1940).
105. Friedrich, K., U. S. Patent 2,212,470 (1940).
106. Daimler, K. (to I. G. Farbenind. A.-G.), U. S. Patent 2,232,053 (1941).
107. Urquhart, G. G. (to National Foam System, Inc.), U. S. Patent 2,269,958 (1942).
108. Ratzer, A. F. (to Pyrene-Minimax Corp.), U. S. Patent 2,324,951 (1943).
109. Ratzer, A. F. (to Pyrene-Minimax Corp.), U. S. Patent 2,361,057 (1944).
110. Bagley, T. J., and Levin, D. (to R. M. Hollingshead Corp.), U. S. Patent 2,365,619 (1944).
111. Tresise, D. J., and Ratzer, A. F. (to Pyrene Development Corp.), U. S. Patent 2,368,623 (1945).
112. Levin, D. (to Chemical Concentrates Corp.), U. S. Patent 2,405,438 (1946).
113. Urquhart, G. G. (to National Foam System, Inc.), U. S. Patent 2,413,667 (1946).
114. Keil, H. L., and Ingraham, J. S. (to Armour and Co.), U. S. Patent 2,431,256 (1947).
115. Perri, J. M., and Hazel, J. F., *Ind. Eng. Chem.*, **38**, 549 (1946).
116. Perri, J. M. (to National Foam System, Inc.), U. S. Patent 2,470,719 (1949).
117. Ratzer, A. F. (to Pyrene Co., Ltd.), U. S. Patent 2,481,875 (1949).
118. Busse, W. F., and Dailey, J. P. (to General Aniline & Film Corp.), U. S. Patent 2,506,062 (1950).
119. Busse, W. F., Lambert, J. M., and Debye, P. P. (to General Aniline & Film Corp.), U. S. Patent 2,514,310 (1950).
120. Swift, C. K. (to MacAndrews & Forbes Co.), U. S. Patent 2,515,276 (1950).
121. Keil, H. L., Hills, C., and Ingraham, J. S. (to Armour and Co.), U. S. Patent 2,521,582 (1950).
122. Busse, W. F., Lambert, J. M., and Debye, P. P. (to General Aniline & Film Corp.), U. S. Patent 2,529,211 (1950).
123. Moilliet, J. L., and Todd, W. (to Imperial Chemical Industries, Ltd.), British Patent 469,325 (1937).
124. I. G. Farbenind., A.-G., British Patent 460,596 (1937).
125. Sthamer, R., British Patent 476,552 (1937).
126. British Patent 524,278 (1940).

127. Daimler, K., Reidelsberger, W., and Paquin, M. (to I. G. Farbenind., A.-G.), German Patent 668,276 (1938).
128. Paquin, M. (to I. G. Farbenind., A.-G.), German Patent 681,158 (1939).
129. Ratzer, A. F. (to Pyrene Co., Ltd.), British Patent 517,767 (1940).
130. Davis, G., and Clark, N., British Patent 571,686 (1945).
131. Migray, E. (to Textil, Kft), Hungarian Patent 127,727 (1941).
132. Von Blanquet, O., German Patent 719,486 (1942).
133. Tresise, D. J., and Ratzer, A. F. (to Pyrene Co., Ltd.), British Patent 559,503 (1944).
134. Mattin, H. E., and Timpson, L. G. M. (to Pyrene-Minimax, Ltd.), Canadian Patent 417,315 (1943).
135. Scheflon, L., and Brown, J. C. (to Pyrene Development Corp.), Canadian Patent 435,733 (1946).
136. Schoenberg, G. (to A.-G. für technische Neuheiten), Swiss Patent 259,609 (1949).
137. Pyrene Co., Ltd., British Patent 580,070 (1946).
138. I. G. Farbenind., A.-G., French Patent 781,818 (1935).
139. Kirstahler, A. (to Henkel & Cie.), German Patent 650,919 (1937).
140. Henkel & Cie, G.m.b.H., French Patent 790,831 (1935).
141. I. G. Farbenind., A.-G., French Patent 789,327 (1935).
142. Böhme, H. Th., French Patent 779,096 (1935).

13. FROTH FLOTATION

ROBERT B. BOOTH

American Cyanamid Co., Stamford, Conn.

Section 1. *Flotation*, or more specifically *froth flotation*, has been defined by Gaudin[1a] as a process of ore concentration involving the segregation of the minerals in an ore into *concentrates* containing the valuable minerals and a *tailing* containing the gangue components of the ore, which are usually worthless.

To effect such beneficiation[2a] ores are ground in water to liberate the valuable minerals from gangue. The resulting ore pulp is conditioned with various chemicals including froth-producing compounds and agitated in flotation machines which introduce and disperse air in the form of fine bubbles throughout the pulp. The bubbles collect at the surface of the pulp as a froth in which the valuable minerals are collected as concentrates and are removed by skimming or by overflowing the froth from the flotation cell. Gangue minerals remain in the body of the pulp and are removed from the operation as a tailing product. The concentrates thus obtained may be upgraded further by refloating with or without additional chemicals, as required, to yield final mineral concentrates suitable for direct use or for further refining. The entire process is a continuous one.

It is obvious that flotation may be applied to accomplish the inverse of the above-described process. In the case of certain ores, by the proper choice of flotation chemicals gangue minerals may be concentrated and removed in the froth to be rejected, thus allowing the recovery of the valuable mineral product as underflow from the flotation machine. It is immediately apparent that the creation and maintenance of a froth to serve as a separating medium at the surface of the pulp is one of the important phases of the process.

In industries other than mineral dressing, froth flotation has found some commercial applications in the clarification of liquids, the removal of waste materials from various solutions, and recovery of certain industrial products[2b, 4]. The method has been applied success-

NOTE. The writer wishes to acknowledge the helpful advice extended to him during the preparation of this chapter by the staff of the Mineral Dressing Division of the Research Laboratories of the American Cyanamid Company at Stamford, Conn.

fully for the continuous removal of fine and difficulty filterable solids suspended in large volumes of liquid; such applications include the clarifying of rayon spinning baths and treatment of water-soluble oils used in grinding operations[5].

Flotation Chemicals

Section 2. Flotation requires the use of chemicals which are added to the ore pulp for the following specific purposes:

(a) *Frothers* to produce a froth of desired characteristics, which acts as a separating medium in which minerals are collected and separated from the pulp.

(b) *Promoters or collectors* which alter the surfaces of the minerals to be floated so as to cause them to adhere to froth bubbles, thus promoting the flotation of the minerals and collecting them into the froth as a concentrate.

(c) *Modifiers* which also change the surfaces of minerals so as to modify their amenability to flotation with a particular promoter-frother combination. These agents may be activators for slow floating minerals, depressants for sulfide minerals in differential flotation operations designed to separate one sulfide from another, inhibitors of the flotation of gangue minerals in both metallic and nonmetallic ores, pH regulators, and the like.

A discussion of the action of collectors and modifiers on the surfaces of minerals[1b, 2c, 3a] lies outside the scope of a chapter devoted to the application of froth and frothing agents in the flotation process. However, in practice the efficiency of a frother used in a mineral separation will be judged not on its frothing ability alone but in terms of mineral recovery and grade of the mineral concentrates, factors generally dependent on the type of collector and modifier used and the cooperative part played by the frother in conjunction with these reagents. A brief study of the development of flotation reagents serves to emphasize this point.

Section 3. The history[2b, 3b] of the development of flotation processes and chemical agents may be divided into two periods[1c]:

1860 to 1920: Oil Flotation
1921 to date: Chemical Flotation

Early in the first period it was observed that the wettability of sulfide and certain oxide mineral surfaces was changed by agitating ore pulps

with large quantities of fatty and oily materials, frequently as high as 10 to 20 per cent based on the weight of the ore. This treatment, known as bulk oil flotation, segregated the sulfide and oxide constituents of the ore in an oily layer and thus allowed separation of these fractions from the gangue constituents and the water. This separation was improved by the use of various modifiers such as acids and certain salts[6]. The buoyant effect of oils for sulfide-oxide minerals was supplemented by the introducing of gases into the ore pulp first by reaction of acids on the suspended sulfides or carbonates[7], by electrolysis of water, or by subjecting the pulp to vacuum[8], by heating[9], by direct introduction of air by means of agitators, porous media, and submerged pipes[1c]. Thus, air became a substitute for oils as a buoyant medium and it was soon established that large quantities of oils were not needed. Oil consumption dropped to less than 1 per cent based on the weight of the ore[10].

The reduction in oil requirements focused attention on the fact that there were differences in the frothing-collecting properties of different oils. Specific frothing agents such as alcohols, ketones, esters, and fatty acids[11] were recommended, indicating that frothing properties were being associated with definite types of chemicals and chemically functioning groups (OH, CO, COOR, COOH, etc). For general use as frothers monohydroxylated compounds such as the higher alcohols, cresols, and pine oils were adopted.

Toward the end of the first historical period, as indicated above, it was recognized that certain types of nonfrothing oils, particularly those containing sulfur, either naturally or added by direct sulfurization, were promoters for sulfide and oxide minerals.[12] In 1921 certain definite chemicals, nonoleaginous in nature, and containing nitrogen or sulfur (e.g., naphthylamines, toluidines, and thiocarbanilide) were established as promoters for metallic ores[13, 14]. This was followed in 1924 by the application of water-soluble xanthates as collectors[15], which ended the use of oily materials as originally employed in the early applications of flotation and marked the start of chemical flotation as known today. Xanthates as the sodium and potassium salts have found wide use, and other water-soluble collectors such as alkyl and aryl dithiophosphates[16] and certain mercaptobenzothiazole derivatives[17] later were developed as collectors for treating ores containing metallic sulfide and oxide minerals. In spite of the marked trend toward promoters showing water solubility, hydrocarbon oils are employed on readily floatable minerals. Also oily type collectors such as

certain dithiophosphates and the xanthoyl formates (reaction products of a xanthate and ethyl chlorocarbonate and related compounds)[18] have found a definite place in the field, and thiocarbanilide, a solid promoter showing very limited solubility, still finds some application.

In pulps of metallic ores certain of the above promoters will produce a froth, generally insufficient to carry the concentrate of floated minerals. Accordingly the same compounds, alcohols, cresols, pine oils, etc., developed as frothers in the early period of flotation, are applied for this purpose.

Section 4. Flotation methods have been extended to treat various nonmetallic ores first in the separation of nonsilicates from silicate minerals and later in the flotation of silica and silicates[97]. In these applications the main types of promoters to find general use are:

Anionic Promoters:

(a) Fatty acids, resin acids, combinations thereof such as found in tall oil, naphthenic acids, and related compounds of petroleum origin; also the sodium and ammonium soaps of such compounds.
(b) Sulfonated compounds, particularly certain petroleum sulfonates and related surface-active materials.

Cationic Promoters:

(a) Long-chain (e.g., 12–20 carbon atoms) amine salts, usually the acetates.
(b) Certain modified amine derivatives.

The fatty acid and soap type collectors find use generally for the flotation of alkaline earth minerals typical of which are calcite, apatite, collophanite, barite, fluorite, magnesite, scheelite, and the like; oxide minerals and salts such as sodium and potassium chloride also respond to certain of these promoters. The main applications of the sulfonated reagents are in the flotation of oxidized iron minerals from low-grade iron ores, iron-bearing contaminants from glass sands and feldspars, talc, garnet, kyanite, barite, and manganese carbonate[75, 78, 85]. The amines and allied cationics find their main use in the flotation of silica from phosphate and also in the treatment of feldspars and other silicate minerals[68, 69, 70].

The effect of the above chemicals as promoters for both metallic and nonmetallic minerals has been rendered more specific by the use of various modifiers which act in flotation as described generally in section 2. It will be sufficient for the purpose of the present chapter to list briefly some of the more important modifing agents:

Acids and alkalies for pH adjustment and control.
Cyanides, usually sodium or calcium cyanide, as zinc depressants in lead-zinc separations.
Copper sulfate, as activator for sphalerite.
Lime, as depressant for pyrite in treatment of copper ores.
Sodium silicate, commonly used as a dispersing-depressing agent.
Hydrofluoric acid as quartz depressant in feldspar flotation.
Dextrin as depressant for carbon and graphitic material in sulfide flotation; also used on talcose material.
Starch as depressant for iron oxide minerals.
Dyes as depressants for carbon and insolubles in sulfide flotation.
Tannic acid and quebracho as depressants for lime-bearing minerals in fluorite, scheelite, and magnesite flotation.
Sodium sulfide, as a sulfidizing agent for oxide minerals such as lead carbonate and in the flotation of oxidized zinc minerals with amine reagents[98].
Zinc sulfate as a zinc depressant in lead-zinc separations; may be used with cyanides.

The Function of Froth in Flotation

Section 5. The term *froth* or *flotation froth* rather than *foam* is generally applied to the mass of mineralized bubbles at the surface of the ore pulp in a flotation cell. This usage is in keeping with the slight differences in the dictionary definition of *foam* and *froth*, the latter term implying a certain degree of lightness or instability in the bubble aggregate. It is also in keeping with general operating practice, where the froth forms continuously in the flotation machine to be skimmed off at the pulp surface and then breaks down readily to allow its mineral load to be flushed along with water (partly from the breakdown of the froth itself and partly added) to subsequent upgrading operations by reflotation and eventually to recovery steps such as thickening and filtering. The flotation operator usually associates the term *foam* with the more closely knit, more permanent bubble aggregates such as those which are formed by certain strongly surface-active chemicals. Such conditions are encountered occasionally in flotation but are avoided whenever possible. The characteristics of various flotation froths will be discussed later in the chapter (sections 12–14).

The function of the froth column at the surface of the pulp as a

separating and concentrating medium in flotation is shown in Fig. 61[2d]. By the combined agitating and aerating action of the flotation machine (see section 20), ore pulp is directed toward the froth column which overlies the surface of the pulp. The separation of the valuable minerals (black in the diagram) from the gangue particles (light colored in the diagram) takes place as indicated. The concentration of the dark grains increases in the upper portions of the froth column; this may be confirmed by withdrawing and assaying mineral samples from different levels in the pulp and the froth column. For example, it has been shown in the flotation of a copper ore that the copper

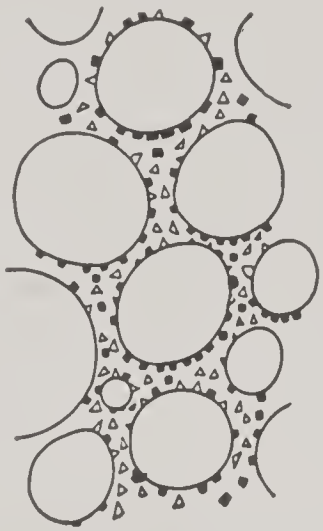


FIGURE 61. Separation of ore (dark particles) from gangue (light particles) Reprinted with permission from Taggart's "Handbook of Mineral Dressing," 1948, John Wiley & Sons, Inc.

content of such samples has varied thus: 0.67 to 0.76 per cent Cu in the pulp body, 0.77 per cent Cu at the froth-pulp interface and 2.07, 4.70, 12.43 per cent Cu at successively higher levels in the bubble column, and finally 38.8 per cent Cu at the froth surface[2d]. It will be apparent from the diagram that the frothing agents tending to produce a closely knit froth will tend to produce a high mineral recovery by carrying a heavy mineral load, while a more loosely textured froth will aid in the dropping out of insoluble gangue from the mineral concentrate.

Section 6. In flotation practice a variety of froth conditions are encountered which are influenced by the type of frother and collector used, the type of ore solids present, the presence of mineral slimes,

pH of the pulp, and dissolved salts. The function of a frothing agent to provide a separating medium is probably best illustrated in the flotation of sulfide ores, where a froth column of 1 to 2 inches (or deeper) frequently forms and carries a well mineralized layer at its surface; such a froth condition allows removal of mineral load to a barren froth practically uncolored except for a small quantity of gangue slimes. The same condition also is noted in some instances in the flotation of nonmetallics. Froths range from this more or less optimum condition to those of lower volume and to heavily flocculated oily curds held up by a thin cushion of bubbles of sufficient thickness to allow the mineral agglomerate to be scraped from the pulp surface. This condition is occasionally noted in sulfide work and is frequently noted in the flotation of nonmetallics where frothing is observed to virtually stop when the mineral load has been removed; such froths occur quite commonly where a material added as a collector, e.g., a fatty acid or sulfonated compound, possesses froth-producing properties as well as collecting properties.

Section 7. Froth-producing substances used in flotation practice may be placed in two main classes:

(a) *Frothers*—Compounds added for the specific purpose of creating a froth; such compounds do not have broad collecting power and usually require the addition of a promoter (usually a compound showing limited frothing power) to achieve desired recovery of mineral values. Such frothers are commonly used in the flotation of sulfide minerals.

(b) *Frothing Collectors*—Compounds added primarily to promote the flotation of minerals but which frequently also produce sufficient froth to support the mineral concentrate. Such cases are quite common in nonmetallic flotation. This frothing action may be supplemented, if such is required, by adding specific frothers as defined in (a) above.

The above division is commonly made by those working in the field of flotation, and compounds in the second class are thought of as collectors although they exhibit frothing properties. In keeping with this practice the term *frother* in the following discussion will be applied to chemicals of the first class. The division is a flexible one, since many cases may be cited where a frother shows a marked tendency to promote certain minerals and where the use of a frother along

with a collector showing frothing properties is necessary for producing optimum frothing and desired separation. This serves to emphasize the cooperative roles played in practice by frothers and collectors in flotation.

Properties of Flotation Frothers

Section 8. A large number of organic chemicals are potent froth producers, but this property is by no means the only factor governing the choice of a frothing agent for flotation use. The frothers in most general use at the present time show the following characteristics[1b, 96].

(a) Form in low concentrations a froth of adequate volume which allows separation of the floated mineral concentrate from the ore pulp, but which exhibits limited stability and thus breaks down readily on removal from the flotation machine.
(b) Are heteropolar organic compounds consisting of one or more hydrocarbon groups attached to one polar group.
(c) Have limited solubility in water (0.2 to 5.0 grams/liter), but show ready dispersibility in aqueous ore pulps.
(d) In the optimum should exhibit low ionization and low promoting activity; promoting power, when evidenced, should be specific for the minerals to be floated.
(e) Show low sensitivity to the pH changes and salt contents encountered in flotation operations.
(f) Are readily available at low cost.

As a direct corollary to (c) above, frothers should not only show low promoting power because of relatively low chemical activity but also should provide a froth of suitable structure to aid in the elimination of gangue particles particularly in cases where slimy gangues are encountered.

Section 9. As indicated previously, the chief compounds employed as frothers in flotation are alcohols, pine oils, and cresylic acids. The active frothing constituents of these agents are monohydroxylated compounds such as alcohols or alkyl phenols and thus the main polar grouping utilized in practice is the hydroxyl group (OH). Recently alkyl (1–4 carbon atoms) ethers and phenyl ethers of propylene and polypropylene glycols have been applied[19]. Also eucalyptus oils and camphor oils have been used.

The following relations of chemical constitution to frothing power

have been pointed out in compounds currently used as flotation frothers[96].

(a) A normal alcohol has higher frothing power than its isomers.

(b) Aliphatic alcohols show higher frothing power than corresponding aromatic alcohols; saturation of the double bonds in the aromatic compound improves and approximately equalizes its frothing power with that of the corresponding aliphatic alcohol.

(c) The addition of the methyl group (CH_3) to the benzene ring of a phenol improves frothing power; further lengthening of the side chain gives only small increases in frothing power.

(d) An increase in the number of double bonds in an aromatic alcohol gives at best only a slight increase in frothing power.

(e) An increase in the number of double bonds in a terpene alcohol improves frothing power; saturation of double bonds decreases frothing power.

(f) Small quantities of impurities influence frothing power markedly.

(g) Froth structure and stability depend on the polar grouping and structure of the frother molecule.

(h) Since limited stability is desired, the hydrocarbon group must be branched, should contain no more than 8 carbon atoms in a single chain or branch, and should be distributed asymmetrically over the whole molecular structure.

Frothing characteristics are associated with other compounds[20] exhibiting in their structures the following functional groups: ketones (CO), aldehydes (CHO), nitriles (CN), esters (COO), amides ($CONH_2$), fatty acids (COOH), amines (NH_2), sulfonates (SO_3H), and sulfates (OSO_3H). Ketones are present in certain of the alcohol frothers[26]. Collecting properties are associated with the amines, fatty acids, and sulfonated-type reagents and accordingly such compounds may be considered to be members of the frothing collector class mentioned above. These compounds frequently produce sufficient froth in certain pulps so as not to require the addition of specific frothing agents, but, as pointed out above, it is common practice in many operations to use frothers in combination with the collectors exhibiting frothing properties.

Section 10. Most of the frothers in practical use show limited solubility in water. The recent introduction of the above-described

alkyl and phenyl ethers of propylene and polypropylene glycol[19] provides water-soluble frothers, which are reported to exhibit low collecting power.

The nonpolar portion of a compound plays an important part in its frothing properties. In the most widely used frothers where limited solubility is an influence, it is, of course, the nonpolar group which controls this factor. Thus, in the case of the aliphatic alcohols, for example, there is an optimum range of chain lengths, 5 to 8 carbon atoms, for the frothers in current use[26]. Also in the case of cresylic acids, frothing properties are indicated to vary with the boiling range of the acids, which increases with length of the side chain in the benzene ring in the nonpolar portion of the frother molecule[21]. Likewise in certain water-soluble, froth-producing compounds the inclusion of several water-solubilizing groups in the hydrocarbon part of the molecule modifies markedly the suitability of the compounds as flotation frothers.

Mention of such requirements as limited solubility and low chemical activity under the usual conditions prevailing in the flotation cell serves to bring out the similarity of frothers to hydrocarbons in collecting action. While hydrocarbons contain no active chemical grouping capable of attachment to the mineral to be floated, these compounds by virtue of their oily nature impart water repellency to minerals as indicated in the above brief consideration of the historical development of flotation agents. Likewise the monohydroxylated frothers show collecting power for certain minerals, for example certain readily floatable sulfide minerals and minerals tending to present a naturally occurring, water-repellent surface such as molybdenite, graphite, talc, mica, etc. This collecting action appears similar to that of the hydrocarbons and frequently is enhanced by the auxiliary use of hydrocarbons with frothing agents. Also the hydrocarbons, either naturally present in frothers, for example the terpenes present in pine oils, or those deliberately added in practice to alcohols and cresylic acids, act as froth stabilizers and give improved recoveries over those obtained with the active frothing constituents of such mixtures used alone[50]. Other oily compounds such as creosotes, tar oils, and the like are used in conjunction with frothers to increase the capacity of froths for coarse size minerals and middling particles.

Section 11. Promoters would be expected to be froth producers or at least influence the frothing action of the specific frothers as indi-

cated by a comparison of the heteropolar structures of both types of compounds in the following type formulas:

Agent	Formula
Frothers (alcohols, cresols, etc.)	R—OH
Sulfide promoters (xanthates, dithiophosphates, etc.)	ROC(=S)—SNa RO \ P—SNa RO S
Nonmetallic promoters (fatty acids, soaps, sulfonates, sulfates, amines, etc.)	RCOOH; RCOONa RSO_3Na; $ROSO_3Na$ RNH_2

With the exception of the hydroxyl group the above-listed polar groupings impart selectivity in collecting power toward a specific class of minerals. Because of the weakly ionized and relatively inactive hydroxyl group (under usual flotation conditions), frothers may be expected to show relatively low collecting power; in fact, where they do exhibit collecting power it is for portions of the ore or for specific minerals which are easily floatable. Thus, gangue minerals are not generally promoted. Selectivity either by nonpromotion of gangue or by providing a froth texture suitable for allowing the elimination of unwanted fine gangue is an important factor in the choice of a frother for a particular use. Such selectivity allows control of both frothing and collecting by adjusting accurately the separate chemicals added for these purposes. However, there are many instances where a relatively large proportion of the minerals in an ore will be amenable to flotation with a frother alone and with simultaneous high rejection of gangue; in such cases operators will, if possible, utilize this selective frothing-promoting power by adding lower quantities of promoters to effect maximum recovery. Sulfide promoters of short chain length are generally nonfrothers or at best not potent froth formers. Such compounds of longer chain length are more potent in this regard with some frothing noted at chain lengths of 4 to 5 carbon atoms. Auxiliary frothers usually are required with these promoters. The dicresyl dithiophosphates in the form of the technical grade products applied

in flotation practice are frothers and frequently it is possible to use these compounds for this purpose, while utilizing their promoting properties at the same time; also these compounds are used as frothers in combination with nonfrothing collectors. The xanthoyl formates, being oily in nature, are not froth formers but in combination with auxiliary frothers, especially certain dithiophosphates, produce froth structures which give high mineral recoveries.

The frothing-collecting action of fatty acids and their soaps, the sulfonated reagents, amines, and other cationics has been discussed above and, as was indicated, in many cases no additional frothing agents are required in flotation operations employing such agents. Voluminous frothing is frequently produced by these compounds and in certain cases requires the use of hydrocarbons to control the volume of froth and modify its structure. On the other hand specific frothers such as the alcohols, pine oil, etc., are commonly used in nonmetallic flotation in conjunction with the above collectors; these frothers are used to increase froth volume in certain cases or to enhance recovery or selectivity. In the treatment of nonmetallics, anionic and cationic promoters frequently produce adequate frothing during the first stages of flotation but require the addition of a frother during the latter stages, as is illustrated in laboratory batch testing where the addition of a frothing agent toward the end of the float facilitates the removal by skimming of the last portions of the concentrate. Though the fatty acids, soaps, sulfonates, and amines frequently are potent frothers, the promotion of gangue minerals by such compounds and the simultaneous lowering of concentrate grade generally preclude their use in sulfide flotation work; on occasion certain of these agents are employed in small amounts as auxiliary frothers but such is not common.

A Comparison of the Main Flotation Frothers

Section 12. The composition and comparative frothing action of the main frothers currently used in flotation practice, i.e., pine oils, cresylic acids, and the higher alcohols, will be discussed briefly.

Pine oil is obtained by the steam distillation and/or solvent extraction of wood chips of southern pines, particularly from pine stump wood. The composition of a pine oil commonly used in flotation is given as[22, 23]:

Components	Percentage
Tertiary alcohols, mainly α-terpineol with small amounts of β-terpineol, terpinen-4-ol, and dihydro-terpineol	55–65
Secondary alcohols: borneols and fenchyl alcohols	10–20
Ketones; fenchone and camphor	5–10
Ethers; anethole and estragol	5–10
Hydrocarbons; monocylic terpenes, such as terpinolene; dipentene, camphene, and pinene	10–20
Moisture	0.4
Total alcohols	75

Beta-terpineol and fenchyl alcohol are indicated in frothometer tests to be the most potent frothers and to have about the same frothing power; next in this respect are alpha-terpineol, borneol, and camphor and these are about equal in frothing power. The remaining components are weaker frothers and while the hydrocarbons present are ineffective frothers, these compounds in combination with the more potent frothing constituents produce generally improved froths and enhance the specific collecting power for certain sulfide minerals. Synthetic pine oils may be prepared from turpentine by chemical treatment and the resulting products are reported to be practically identical in frothing properties with natural pine oil[22].

Section 13. *Cresylic acids* used as flotation frothers[21] first were obtained from the by-product coking of coal and since 1937 from the thermal cracking of petroleum. At the present time the petroleum cresylics are most widely used. These frothers are recovered by caustic extraction of phenolic fractions to remove entrained oil, followed by acidification of the sodium phenolate solution to separate out the cresylic acids which are fractionally distilled. Formerly considered as mixtures of ortho-, meta-, and para-cresols, cresylic acids in recent years are regarded as mixtures of the three isomeric methyl phenols, six isomeric xylenols, and other higher boiling phenols. The coal tar and petroleum cresylics have been shown to contain similar compounds particularly in the lower and middle boiling ranges but in varying quantities. The main impurities in such frothers are small quantities of phenol, water, neutral oils, nitrogen bases such as pyridine derivatives, and sulfur-containing compounds (e.g., 0.3 to 1.0 per cent S) such as thiophenols which are promoters for sulfide minerals. Frothing characteristics vary somewhat with the boiling range of the acid, the lower ranges producing a light froth as compared to

the more lasting froth produced by the higher boiling ranges. The higher boiling types are more widely used in practice.

A study of the relative flotation activity (frothing-promoting power) of the constituents of crude cresylic acid on lead and zinc ores both in the presence and absence of xanthate promoters has indicated that meta-cresol is most potent and that as a class the cresols are stronger than other phenolics present[24]. Certain xylenols (boiling range 218–228°C.) have been used as frothers[25].

Section 14. The main *alcohols* currently used as frothers are in the 5 to 8 carbon atom range. These frothers include mixed amyl alcohols, methyl isobutylcarbinol, certain heptanols, and octanols such as capryl alcohol. Mixtures of primary and secondary alcohols of 6 to 8 carbon atoms with ketones and esters are also effective frothing agents[26]. Higher alcohols in the 10 to 12 carbon atom range produce suitable froths of good volume and texture, provided the chain is branched sufficiently. These alcohols are currently higher in price than those of shorter chain length and have not found wide use.

The efficiency of a frother is not judged entirely on frothing action alone but rather on the combined effect of a frother-collector or frother-collector-modifier combination as evidenced by mineral recovery and grade of concentrate. Consequently a change in the type of collector in use may entail a change in the type of frothing agent as well. Frothing is affected by a number of variables, of which some of the most apparent are pH, dissolved salt content, degree of grinding, presence of slime fractions, type of slimes, etc. These factors obviously vary widely depending on the type of ore treated and, as an example, a frother may operate well only over a narrow pH range for one ore but give good froth over both acid-alkaline ranges in another ore. Accordingly, it is rather difficult to make a firm comparison in the performances of the commonly used frothers listed above, since their action will vary from one flotation operation to another. An attempt will be made to do this with the realization that there may be some just disagreements with the following summary in the light of experience on specific ores.

Pine oil forms a small-bubble, closely knit froth which breaks readily. A marked decrease in volume and an effervescent froth result when excessive amounts of this frother are used. Though on certain ores pine oil has a tendency to be somewhat less selective than other

frothers, its froth structure is conducive to high recoveries of mineral values.

Cresylic acid forms a well-knit froth resembling that of pine oil but of somewhat larger bubble. Excessive quantities cause effervescence and a decrease in volume. Cresylic acid has good promoting powers for certain sulfides and is frequently chosen because of this factor.

The alcohol frothers produce froths of larger bubbles and looser structure than pine oil and cresylic acid, particularly in the short chain lengths. The use of large quantities of these frothers tends to tighten up the froth structure and produce finer bubbles but does not tend to flatten or kill froth to the same degree as noted for pine oil or cresylic acids. In certain pulps the froth has a tendency to diminish in volume after a short time unless further additions are made, a factor considered to be an advantage in some differential flotation processes, where the second flotation circuit may require a different reagent combination than the first. The loose froth structure allows the elimination of fine gangue, and the alcohol frothers frequently are preferred with various slimy ores.

The above comparison summarizes some of the most prominent characteristics of the commonly used frothers. It will be clear from the above that laboratory and even mill trials on an ore pulp are required before a firm choice of a specific frother for a particular flotation separation can be made. Frothometers[23, 95] for testing frothers have been used and give some idea of frothing power and stability; they do not show up the effect of the variables indicated above as existing in actual ore pulps.

Other Compounds as Frothers

Section 15. A brief summary of various other products which have been recommended as specific flotation frothers is given below. These materials are generally of definite chemical composition or well defined mixtures.

The lower alkyl (1 to 4 carbon atoms) and the phenyl mono-ethers of propylene and polypropylene glycols were introduced recently as flotation frothers[19] and currently are being evaluated at several flotation plants. Such compounds may be prepared under anhydrous conditions by the reaction of propylene oxide on an alcohol (1 to 4 carbon atoms) or phenol at 80 to 130°C. under pressures of 20 to 30 psi with 0.5 to 1.0 per cent sodium hydroxide as catalyst. The reaction product is neutralized with acid and distilled to remove volatile components

leaving the ethers of propylene and polypropylene glycol as distillation residue. Reaction mixtures may be used without purification. As compared to frothing agents such as pine oil and cresylic acids, these mono-ethers are reported to show equivalent frothing power with lower quantities of frother and also to exhibit a high degree of selectivity. The mono methyl ether of tripolypropylene glycol is highly soluble in water and is an active frother. The use of such compounds represents a departure from the concept that frothers should have limited solubility in water. The lower alkyl monoethers of polypropylene glycol, as typified by "methoxytripropylene glycol," form a small bubble froth which resembles that produced by certain surface-active agents. These froths are persistent in the flotation cell but break readily on being skimmed off. A closer knit structure and voluminous frothing results if excessive quantities are used but, because of water solubility, effervescent froths are not produced.

Various phenol derivatives closely related to the cresylic acids such as high-boiling coal tar distillates and creosotes have been applied as frothing agents[27]. Completely hydrogenated tar acids are reported to show a marked increase in froth volume over that exhibited by the usual tar acid frothers. For example, in a laboratory flotation machine the froth column with phenol and with ortho-, meta-, and para-cresols ranged from a trace to 1.25 in. as compared to 0.5 to 2.25 in. with the corresponding hydrogenated compounds[28]. Propyl phenol is indicated to be a good frothing agent[24] as also are alkylated crude low-boiling cresylic acids; such frothers containing alkyl groups of 2 to 5 carbon atoms and particularly the propyl and butyl derivatives are preferred[29].

While monohydroxy compounds are the chief frothers in current use, certain products containing two hydroxyl groups are strong frothing agents. For example, tetramethyl ethylene glycol is recommended as a frother[30]. *n*-Hexyl resorcinol is indicated to have frothing properties and *n*-octyl and *n*-nonyl resorcinol have given good results on lead ores[24]. Dihydroxyphenols such as catechol, quinol, resorcinol, orcinol, *n*-amyl resorcinol, iso-amyl resorcinol, and isohexyl resorcinol are poor frothers[24].

Aldehydes, particularly aldehyde condensation products such as aldol, acid condensation products of aldol, polymers such as paraldol, dehydration products such as crotonaldehyde, aldehyde resins from alkali condensations of acetaldehyde, acid-treated aldol, etc., have

been recommended as flotation frothers in the range of 0.2 to 0.5 lb/ton[31].

Ketones, particularly those which are water-insoluble (e.g., dipropyl ketone) are flotation frothers[32]. Condensation products from acetone such as mesityl oxide, phorone and isophorone, and similar condensation products from methyl ethyl ketone froth when added to ore pulps in amounts of 0.1 to 0.2 lb/ton[33].

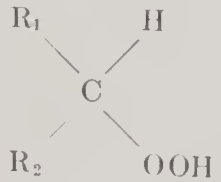
Section 16. Alkyl and alicyclic glycolates, $CH_2OHCOOR$ (R = radicals of 1 to 12 carbon atoms, e.g., isobutyl, cyclohexyl, dodecyl), are described as useful frothing agents in the flotation of sulfide, nonsulfide, and nonmetallic minerals[34]. These frothers also show some collecting properties for certain minerals such as molybdenite.

Secondary and tertiary aromatic alcohols (9 to 12 carbon atoms) have been used as frothing agents[35], including:

8-*p*-cymenol
α,α-dimethylbenzyl alcohol
$\alpha,\alpha,\alpha',\alpha'$-tetramethyl-$\alpha,\alpha$-xylene diol
α,p-dimethylbenzyl alcohol
α-ethyl-α-methylbenzyl alcohol
α-ethyl benzyl alcohol
α,α-dimethylcuminyl alcohol
α-isobutylbenzyl alcohol
α,α,α'-trimethyl-α,α'-*p*-xylenediol

Certain hydroperoxides are reported to be effective frothing agents in the flotation of sulfide, oxide, and nonmetallic ores.

Secondary cyclic hydroperoxides[36] of 6 to 15 carbon atoms (preferred range is 8 to 13 carbon atoms) of formula:



where R_1 = cyclic radical

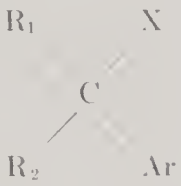
R_2 = cyclic or aliphatic radical

are utilized and may be obtained by oxidation of compounds $R_1R_2CH_2$. Typical are:

α-methylbenzyl hydroperoxide from ethylbenzene
α-methyl-*p*-ethylbenzyl hydroperoxide from *p*-diethylbenzene
diphenylmethyl hydroperoxide from diphenylmethane

Related frothing agents are the secondary cyclic hydroperoxides[36] of formula CHOOH, where the carbon atom is in the ring of a cyclic compound. Such compounds are obtained by oxidation of dipentene, carvomenthene, α- and β-pinenes and other cyclic terpenes, and also other cyclic compounds such as tetrahydronaphthalene, decahydronaphthalene, cyclohexene, and substituted cyclics.

Mono- and di-hydroperoxides such as the α,α-dialkylarylmethyl hydroperoxides also are frothers[37]. These compounds are of formula:



where R_1 and R_2 are alkyl groups; Ar is an aryl or alkaryl group; and X is the hydroperoxy group (OOH).

Typical of these frothing agents are α,α-dimethyl-*p*-methylbenzyl, α,α-dimethylbenzyl, and α,α-dimethyl-*p*-isopropylbenzyl hydroperoxides obtained by the oxidation of *p*-cymene, cumene, and diisopropylbenzene[38], respectively. From the latter compound, $\alpha,\alpha,\alpha',\alpha'$-tetramethyl-*p*-xylene dihydroperoxide may be obtained also. The aryl or alkaryl group may be derived from compounds such as benzene, naphthalene, anthracene, phenanthrene, and various related alkaryl substituted products.

The above hydroperoxides are reported to show virtually no collecting properties.

Section 17. Trialkoxy paraffins (e.g., 1,1,3-trimethoxypropanes) and similar propoxy and isopropoxy compounds are stated to be good frothers[39] as are similar butane derivatives. These frothing agents are claimed to be more powerful and more selective than conventional frothers and to show less tendency to flatten the froth column, if an excess is used. The reaction product of crotonaldehyde and ethyl alcohol is a preferred frother of this type.

Tetraalkoxy paraffins with 2 to 5 carbon atoms in the paraffin chain and a pair of alkoxy radicals selected from methoxy, ethoxy, normal propoxy, and isopropoxy on the terminal atoms (e.g., 1,1,

2,2-tetraethoxyethane, 1,1,5,5-tetraethoxypentane, etc.), are reported to be effective frothing agents[40].

Pyridine, quinoline, and various nitrogen bases including those obtained from petroleum have frothing properties[41] and tend to be specific promoters for certain sulfides. For example, petroleum nitrogen bases such as mixtures of alkylated heterocyclic nitrogen-bearing compounds boiling between 120–630°F are frothers-promoters for zinc sulfide ores[42]. Lower quantities of the conventional frothers are reported to be required when materials of this type are used.

The water-soluble salts of cymene sulfonic acid, e.g., sodium *p*-cymene sulfonate, are reported to act as selective frothers in the flotation of lead, zinc, and copper ores[43].

Some Compositions with Frother-Collector Properties

Section 18. Miscellaneous compounds such as naphthalene in solid form or as a solution in hydrocarbons[44]; terpene hydrate[45]; alkyl thiocyanates[46]; certain esters; water-soluble half ester salts such as sodium monoabietyl, mono-octyl, monodecyl, and mono-octadecylphthalates[47]; and aliphatic dinitriles[48] are mentioned as frothers and collectors. Mixtures of primary and secondary unsaturated amines have frothing as well as collecting properties[49].

Saturated hydrocarbons do not froth and unsaturated hydrocarbons are reported to show limited frothing tendencies[3c]. However, hydrocarbons are naturally present in such frothers as pine oil[22, 23] and are added as extenders and froth stabilizers to the alcohols[50] and cresylic acid frothers. Hydrocarbons in combination with frothers are commonly used in the flotation of readily floatable minerals such as graphite, molybdenite, and coal and also enhance the collecting action of anionic and cationic agents by increasing the water repellency of various nonmetallic minerals. Hydrocarbons are frequently applied for this purpose when slimes are encountered in flotation either by natural occurrence in the ore or formed by abrasion during the flotation operation. In certain floats hydrocarbons serve to control voluminous frothing and improve froth structure.

Other Froth-Producing Materials

Section 19. Various materials, often of indefinite composition, have been used as flotation collectors and certain of these have exhibited frothing characteristics. A brief summary of these products will be given.

Various extracts obtained by solvent or alkali treatment of the naturally occurring petroleum-water mixtures from oil wells, tar oils, sulfur-bearing petroleum oils, shale oils, still residues and gases, wood oils, and tar products have frothing properties and were utilized in the early flotation period. In certain cases the oils thus extracted were recovered by distillation or acid treatment of the alkaline extract and were used as frother-collectors[51].

Products of destructive distillation, oxidation, and cracking processes have found use as frother-collectors. These include the products obtained from the destructive distillation of sage brush[52], oleic acid, cottonseed oil, wood, gas oils, cellulose carbohydrates, bitumen, bituminous coal[53], greasewood[54], and gilsonite[55]. Oxidation products of hydrocarbons occurring in petroleum, shale oil, waxes, and oils obtained from the low-temperature distillation of coal are reported to be frothers; these products contain fatty acids, aldehydes, alcohols, and waxes[56]. Small amounts of petroleum hydrocarbon sulfonates have been used with certain of these products[57].

Alkali-treated wood pitch, rosins, coal and wood tars, creosotes, and shellac found application as flotation oils with frothing-collecting properties during the early period of flotation[58]. In certain cases solutions of these materials in alcohols or hydrocarbons were employed. Also the solids obtained from drying the alkaline aqueous extracts have been used[59].

Fatty acids and soaps are collectors for a variety of minerals and, as indicated, frequently produce sufficient froth volume so that frothing agents such as pine oil, the higher alcohols, and cresylic acid need not be added, or, if required, frequently may be used in small amounts. While the chief agents of this type in current use are tall oil and oleic acid and their soaps, other similar or related materials find a place particularly in nonmetallic flotation; such agents include black liquor soap from the paper industry, alkali resinates, naphthenic acids and their soaps, and the by-products of the refining of fatty acids and glyceride oils (still bottoms, foots, etc.) which are usually applied in saponified or emulsified form[60].

Numerous references to the use of sulfonated and sulfated compounds as frothers and collectors may be found in flotation literature. A variety of such materials has been recommended[61] including sulfonated oils and fatty acids, hydrocarbon sulfonates, refinery sludges, olefin-sulfuric acid reaction products, naphthalenesulfonic acids, alcohol sulfates, alkyl phenol sulfonates, lignin sulfonates, and various

other sulfonated products. Sulfonates frequently find use as emulsifying agents for hydrocarbons and oily promoters such as fatty acids and accordingly aid in the production of froth in certain flotation operations.

Flotation Machines: Operating Principles

Section 20. Patent literature on flotation equipment lists many flotation machines of which only a very small number have found their way into wide practical use. To present information on or even to describe briefly the flotation cells currently employed is beyond the scope of this chapter. Such information is available from other sources[2e] and a summary of the operating principles will be given for the more common types of flotation cells.

These cells are open top vessels through which the ore pulp is conducted continuously and include means for simultaneously agitating and aerating the pulp usually in the lower portions of the cell; means for establishing a quiescent zone in the upper portions of the cell, toward which the pulp is directed by the combined action of agitation and lifting effect of the bubbles and where the bubble aggregate or froth column forms to allow selective separation of the wanted mineral product from the unwanted fractions of the ore; and finally means for removal of the mineral concentrate from the froth column for further treatment and recovery and for removal of the rejected tailing product. The importance of the froth or bubble column as a selective separating medium has been illustrated earlier in this chapter in section 5.

Air was introduced directly into the pulp by agitation in the early period of flotation when large quantities of oil were used but this method of aeration is not in common use in current plant practice. Aeration by cascading or tumbling the pulp was also employed and, though cells of this type were utilized at certain plants, their application has been limited, since only the easily floated ores respond to this type of treatment.

Section 21. The main types of flotation machines which now find widest practical application are two: (1) the pneumatic cell and (2) the subaeration cell. It will be apparent that, since the flotation process depends on aeration, the two types differ in the method utilized in introducing and dispersing air into the ore pulp. The pneu-

matic cells blow air directly into the pulp. The subaeration cells are of two types. In the first a rotating impeller serves as a pump submerged in the ore pulp, which draws in air usually through the hollow shaft of the impeller or through a suction pipe connected to the impeller zone and distributes this air into the pulp. In the second class, air is blown into the agitation zone, usually at the base of the impeller, and is distributed through the pulp by the rotation of the impeller.

Two factors are important in cell design: (1) to provide a volume as large as possible for aerating the pulp and directing it into the bubble column at the surface and (2) to move the pulp through the cell for discharging and also to prevent dead areas in the cell which rob it of effective aerating volume.

Section 22. Fig. 62[2f] and the ensuing discussion which follows closely similar information presented by Taggart[2e] describe the operating principles of several types of flotation cells.

Diagram *A* represents a pneumatic cell in which air is introduced into the pulp through a porous medium forming the bottom of the cell. The early pneumatic cells such as the Callow type[62] utilized canvas and later rubber mats as such porous media to provide fine air bubbles. Aerating media of this type were subject to blinding due to the deposition of carbonates from action of carbon dioxide in the air on the pulp and the accompanying cementation of ore fines. To relieve such clogging the cell had to be emptied at frequent intervals and the aerating medium washed with acid, brushed, or pounded to dislodge the sediment. Diagram *A* indicates that this type of cell makes practically all of its entire volume available for pulp aeration. However, this type of aeration has a tendency to produce large-size bubbles and also is not highly effective for moving pulp through the cells, factors which affect the over-all efficiency of the cell.

The MacIntosh cell[63] was a modification of the porous-bottom cell. The pulp was aerated through a porous medium, canvas or perforated rubber, wrapped around a perforated pipe which rotated near the bottom of a V-shaped vessel, as illustrated in Diagram *B*. Aeration is more efficient and less tendency to blind was noted. Large bubbles and accompanying turbulence in the center of the cell were common in operating practice.

Diagram *C* shows the introduction of air by cascading and the use

of a baffle, *a*, to prevent short-circuiting of pulp; as indicated above, such cells provided a low supply of air and accordingly found limited use.

To overcome the blinding of porous aerating media and the accompanying loss of aerating efficiency, currently used pneumatic cells introduce air by means of pipes which point downward to the bottom of the cell and utilize the principle of the air-lift to aerate and circulate the pulp. The incoming air lifts the pulp, as diagrammed in *D*,

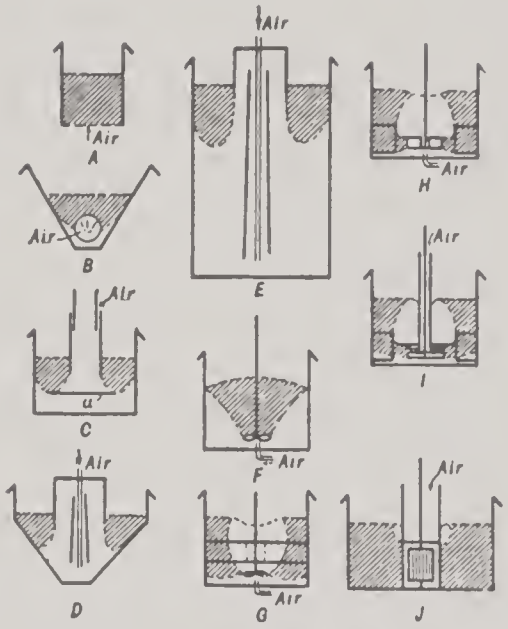


FIGURE 62. Operating principles of some flotation cells. Reprinted with permission from Taggart's "Handbook of Mineral Dressing," 1948, John Wiley & Sons, Inc.

through inclined baffles and directs it through a hood equipped with perforated baffles which provide a quiescent zone in which the froth column may form. A finer dispersion of air, less pulp turbulence, and more efficient movement of pulp through the cell are obtained with some sacrifice of volume available for aeration. The Forrester cell[64] was the first of the air-lift type to find plant-scale application. By modifying the height of the air lift above the pulp level, the type of deflecting baffles above the air-lift and their position and depth in the pulp body, and the size and shape of the housing vessel (see Diagram *E*), a variety of such cells have been created. These include the Hunt, or Hunt-Dunn, and the Steffensen cells.

Section 23. Diagrams *F*, *G*, *H*, *I*, and *J* illustrate subaeration cells of various types and show schematically the effect of various types of impellers and baffles on aeration.

Aeration by means of simple agitation of an impeller is illustrated in Diagram *F*; incomplete coverage of the surface with froth and considerable turbulence because of poor distribution of air are shown.

Diagrams *G*, *H*, *I*, and *J* illustrate the operation of subaeration cells and the effect of their design on the volume of pulp available for aeration. Both types of cells in this class—those obtaining air from an outside blower or by pumping action of the impeller—distribute the supplied air by the agitation of the impeller; control turbulence in the pulp by the use of horizontal grids, vertical baffles, etc.; and thus provide for a quiescent zone in the pulp and supernatant froth column at the surface.

In Diagram *G* the impeller has been reversed from that in Diagram *F* and perforated plate baffles or grids have been inserted above the impeller to break the turbulence in the pulp; the effect on aeration and frothing is apparent by a comparison to Diagram *F*.

Diagram *H* illustrates shrouding the impeller at the top and side baffling to control swirling in the pulp, factors which give finer dispersion of air and are incorporated into flotation cells such as those of the Agitair[65a] and Weinig[65b] types. Similar baffling with top- and bottom-shrouded impellers are used in the Mineral Separation type cell[65c] or the Denver Sub-A (Fahrenwald) machine,[65d] the latter employing a bladed shroud above the impeller to achieve fine dispersion of air.

In the Fagergren machine[65e] the impeller is a vertical rotor of the squirrel cage type which operates under a standpipe extending from above the pulp surface down to a squirrel cage stator whose vertical bars surround the rotor (illustrated in Diagram *J*). Rotation of the rotor draws air down through the standpipe, mixes it with the pulp, and forces this mixture through the bars of the stator, thus causing an intense shearing action and the formation of fine bubbles which rise through the body of the pulp to form the bubble column at the surface. It is apparent that this type of cell makes available for aeration a large proportion of its volume.

Section 24. Time of residence of the pulp in flotation machines should be sufficient to achieve maximum recovery of the wanted

mineral in a flotation concentrate and to allow for the further upgrading of this concentrate by reflotation. Small-scale batch flotation tests on an ore will provide a good estimate of the time requirements and indicate the cell capacity necessary for the continuous treatment of large tonnages of ore. In practice this capacity is provided frequently by arranging several similar cells in series so that the pulp is subjected to the successive agitating-aerating-transporting actions of several mechanisms until the desired recovery is attained and the tailing product discharged. In other cases, several of mechanisms of a unit cell are placed in series within a single vessel.

In a flotation operation involving the separation of one mineral (or group of related minerals, e.g., several copper-bearing minerals in one and the same ore) from gangue, the ore commonly is subjected to a roughing float which is directed to obtaining a concentrate of as high grade as possible and to producing a discardable tailing low in content of the floated mineral. Within limits the emphasis in roughing is on mineral recovery rather than on grade since the rough concentrate may be upgraded (or cleaned) by one or more cleaning flotation steps to achieve the grade in the final concentrate as set by specification and obtain as high a ratio of concentration as possible.

Flotation cells are arranged so that the rough concentrate is flowed directly to cleaning cells; similarly cleaned concentrates may be recleaned as required. The tailing product from the above-described roughing operation is usually pumped to waste. The tailings from cleaning also may be discarded, if sufficiently low in values, but generally they are high enough in grade to warrant reworking and are recirculated (e.g., returned to the roughing float); such return represents a circulating load on the flotation cell in addition to the freshly introduced flotation feed of pulp. Flotation capacity required in cleaning is considerably less than in roughing, since the feed to cleaning is only a portion of the total pulp originally fed to the flotation system.

In the case of ores containing two different valuable mineral constituents differential flotation practice usually is to remove one of the values in a roughing float and to send the tailings from this operation to a separate flotation circuit where the second valuable mineral constituent is recovered.

Flotation chemicals, frothers, promoters, and modifiers are often added prior to roughing in a separate conditioning step in which the ore is agitated with the added agents prior to entering the flotation machine. In other instances the reagents are fed to the pulp just as

it enters the cell or to the first cell in a series operation. Stage feeding of reagents during roughing and cleaning is commonly practiced, if such is required. Frothers frequently are thus stage-fed to maintain adequate froth volume throughout the operation. In many cleaning floats it is unnecessary to add further quantities of reagents, since carry-over on the concentrate or in the accompanying water from the roughing step is sufficient to maintain satisfactory promotion-frothing in the cleaning cells.

Applications of Froth-Producing Agents in Flotation

Section 25. Applications of frothers and collecting agents with frothing properties will be described by means of examples of flotation separations on various types of ores. These examples for the most part are taken from actual operating practice.

Sulfide minerals may be considered as a class. It is general practice to float sulfides by the use of the sulfhydril collectors with suitable modifying agents as needed and the conventional frothers such as pine oils, cresylic acids, the higher alcohols, and certain of the frothing dithiophosphates. Frother consumption is generally in the range of 0.02 to 0.2 lb/ton of ore treated.

Nonmetallic minerals such as calcite in cement rock, fluorite, calcium phosphate, barite, and magnesite are amenable to flotation with anionic-type collecting agents such as fatty acids, soaps, and other similar anionic collectors which frequently provide sufficient froth to support the mineral concentrate so that additional frothing agent is not added. However additions of frothers, particularly the alcohol frothers, are made to supplement the frothing action of the collecting agent in certain floats.

Cement rock is beneficiated by flotation treatment to yield calcite (calcium carbonate) concentrates of sufficiently high grade to allow blending with raw rock, iron oxides, silica, etc., thus giving kiln feeds of composition such that cements of desired characteristics will be produced. On certain Pennsylvania cement rocks containing carbon the practice is to float off a portion of the carbon with an alcohol-type frother, and then float the calcite by the use of oleic acid and, in certain cases, mixtures of fatty and resin acids such as occur in tall oil, in the presence of lignin sulfonates to depress the remainder of the carbon[66]. The promoter is stage-fed during the float along with alcohol-type frothers. Emulsions of fatty acids of various types are used also.

Requirements of fatty acid and frother are 0.5 to 1.0 lb/ton and 0.1 to 0.2 lb/ton, respectively.

Magnesite (magnesium carbonate)[67] responds readily to flotation treatment with oleic acid as collector. Siliceous impurities are first floated off with frothers such as pine oil and methyl isobutyl carbinol or by the use of cationic reagents. The resulting tailings are floated in the presence of oleic acid to concentrate magnesite and tannin compounds such as quebracho for the depression of calcite and dolomite gangues.

Section 26. The *phosphate constituents* from Florida phosphate rock are amenable to flotation with tall oil and reagents of the fatty acid type[68]. The flotation feed is deslimed thoroughly and thickened to allow conditioning at high solids with caustic, heavy fuel oil, and tall oil, and floated to produce a phosphate concentrate which may be cleaned by refloating. The concentrate grade may be raised further by continued cleaning with some sacrifice in phosphate recovery, but practice is usually to refloat by means of cationic reagents[69]. Phosphate concentrates produced as above are treated with sulfuric acid to remove collector coatings and then subjected to flotation with long-chain amine salts such as the acetates or other amine derivatives in combination with hydrocarbon oils such as light fuel oils or kerosene, which remove silica in the froth and leave the phosphate concentrate as a tailing product. This application is the main use for cationic reagents in flotation at the present time. In plant practice both operations are usually conducted without addition of other frothing agents.

Fluorite (calcium fluoride) concentrates are produced[71] from ores containing silicious gangues by flotation with about 1.0 lb/ton oleic acid. Froth provided by the fatty acid collector is usually adequate for these separations.

Barite (barium sulfate) is floated by the use of fatty acids and soaps as collectors in the presence of caustic, sodium carbonate, sodium silicate, and quebracho as inhibitors of lime- and iron-bearing gangues[72]. Recently oil-soluble, water-dispersible petroleum sulfonate reagents have been applied to float barite from iron minerals; sodium silicate is an effective depressant for the iron minerals in such floats.

Scheelite (calcium tungstate) and other tungsten minerals are floated from lime- and silicate-bearing gangues with anionic collectors[73]. Con-

taminating sulfide minerals, if present, are first removed with conventional sulfide promoters and frothers and the resulting tailings treated with quebracho, sodium silicate, and sodium carbonate as gangue depressants and with oleic acid or tall oil as collectors for the tungsten minerals. The tungsten content of such ores is generally low and accordingly a high rejection of gangue is demanded. For this purpose a lacey froth structure is preferred, which will bear up the relatively light tungsten concentrate but at the same time allow the elimination of gangue from the froth column; this is achieved by use of sulfonated hydrocarbon reagents of the detergent and wetting agent type or certain rosin soaps. The sulfonated reagents, though imparting the required froth structure, must be used in small quantities as otherwise depression of tungsten minerals occurs.

Combinations of oil-soluble, water-dispersible petroleum sulfonates and the fatty acids such as those contained in cottonseed oil foots are utilized to float *rhodocrosite* (manganese carbonate) in the presence of caustic soda or sodium carbonate and sodium silicate as depressants for silicate gangue. The use of these sulfonates improves frothing, facilitates visual control of the flotation operation, and gives generally improved metallurgy.

Manganese oxides are floated with fatty acids, soaps, and sulfonated reagents used in conjunction with fuel oils. The harder, more crystalline varieties are indicated to be readily floatable but the fine, amorphous oxides respond to flotation only when extremely large quantities of reagents are employed; consequently low-price promotors such as black liquor soap and fatty acid by-products, along with hydrocarbon oils, are used in these cases.

Section 27. During recent years considerable interest has been shown in the flotation of low-grade *iron ores*, particularly of those ores showing intimate association of iron minerals and quartz gangue. The chief iron mineral in such ores is hematite with some magnetite and varying quantities of other oxidized iron minerals. Several methods of treatment have been suggested and have been evaluated on a pilot plant scale based on the two obvious possibilities of separation, the flotation of iron from quartz and a quartz-from-iron flotation. It has been proposed to float iron directly by first conditioning the pulp with sulfuric acid, desliming and washing, treating with alkali to give

a pH of 8.0 to 9.0, and floating with emulsions of tall oil soaps, sodium resinates, and fuel oil as collectors[74].

Sulfonated anionic collectors of various types also are used[75]. The ore is conditioned in acid circuit with the sulfonated reagent and fuel oil and floated. Typical reagent consumptions are 1.0 to 3.5 lb/ton sulfonate collector with an equal range of fuel oil and 0.5 to 3.0 lb/ton sulfuric acid. The sulfonate type collector usually supplies sufficient froth so that no frother additions are necessary. In certain cases the use of frothers in the latter stages of this float aids in removing the last portions of the floated iron minerals.

Silica is floated from iron by the use of anionic collectors such as fatty acids, resin acids, tall oil, and their soaps in the presence of various modifying agents[76]. Lime and lime with starch in various forms are used for this purpose as also are lime in combination with lignin sulfonates, tannins, alkaline phosphates, alkaline polyphosphates, and portland cement in combination with starch. The presence of the alkali activates the silica and other auxiliary modifiers serve to depress iron into the tailing product during the flotation of the silica. Conventional frothers are used in certain of these floats.

Cationic reagents such as the long-chain amine salts are also used in removal of silica from iron[77]. The circuits employed are usually alkaline, and sodium sulfide, ammonium compounds such as the hydroxide and carbonate, alkali metal hydroxides and carbonates, and acid- and alkali-treated starches are used as modifying agents. Various frothers and particularly the higher alcohol frothers are used in such floats.

Garnet, particularly the almandite variety, is floated by means of fuel oil and various sulfonated reagents[78]. Oil- and water-soluble petroleum sulfonates of the mahogany soap type and the green acid type are used for this purpose, and other sulfonates such as sulfonated fatty acids and glyceride oils also have been recommended. The higher alcohols are used in practice as frothing agents.

Other silicate minerals such as *talc* also respond to sulfonate collectors. *Kyanite* may be floated with sulfonated or fatty acid collectors[79].

The flotation of *ilmenite* (iron titanium oxide) with fatty acids, tall oil, and their soaps[80] forms a basis of separation between ilmenite and apatite in certain ores. The feed is first deslimed and a bulk ilmenite-phosphate concentrate produced in alkaline circuit (sodium

silicate, sodium hydroxide, potassium hydroxide, ammonium hydroxide); this bulk concentrate is conditioned with causticized starch to depress the ilmenite while the apatite is floated off with fatty acids, tall oil, and other related anionic collectors in the form of the free acids or soaps. This method produces ilmenite concentrates sufficiently low in phosphoric anhydride content to allow their use in the preparation of titanium dioxide pigments and provides an excellent example of an application of the flotation method for obtaining close chemical control.

Section 28. *Silica* is floated by means of the cationic-type promotors such as long-chain amines and amine derivatives as indicated above in the description of the treatment of phosphate rock[68,69,70]. These compounds are usually self-frothing, but the standard frothers are used frequently in such separations. The alcohol frothers are indicated to show more selectivity than pine oil and cresylic acids and are often preferred in these operations.

Cationic promotors will float a variety of *silicate minerals* and are used to float feldspars. For the separation of quartz-feldspar, cationics are utilized to float the feldspar while the silica is depressed by the use of hydrofluoric acid[81]. Conventional frothers may be used as desired in such separations.

Iron-bearing minerals such as micas, ilmenite, iron oxide minerals, etc., which are contaminants in glass sands and feldspars are floated off to produce a tailing sufficiently low in iron to allow its use in the manufacture of glass and ceramics. For this purpose fatty acids, resin acids, tall oil, naphthenic acids, and certain sulfonated reagents are used in combination with alkalies and various alkaline earth metal salts[82].

Cationic agents, mainly long-chain amine salts, have been applied to sands and feldspars[83]. A two-step flotation treatment has been recommended, which utilizes first a fatty acid-fuel oil combination as collector in alkaline circuit followed by a second treatment involving the addition of a mineral acid and flotation with a cationic reagent and pine oil as frother; the froth products are discarded. Cationics are also used in a two-step process in which the quartz is first floated off and then conditioned with acid and refloated without additional reagents to make a discardable froth product and a low iron tailing.

Recently sulfonated reagents such as the petroleum sulfonates of

the oil-soluble and green acid types have been applied in combination with fuel oil in acid circuit to remove the iron-bearing contaminants[84].

Section 29. The flotation of *soluble salts* as *sylvite* (potassium chloride) or *halite* (sodium chloride) is conducted in solutions saturated with respect to the soluble constituents of the ore. Potassium chloride may be recovered by direct flotation from halite or by removal of the halite by flotation leaving the potash in the tailings product.

Cationic reagents such as the normal, primary amines of 7 to 12 carbon atoms; straight-chain acyl derivatives of ethylene diamine (the acyl group containing 10 to 18 carbon atoms from such fatty acids as lauric, myristic, and cocoanut oil acids); straight-chain esters (6 to 12 carbon atoms) of glycine; certain phosphonamides; reaction products of amines with sulfur chloride; and chlorinated aminated hydrocarbons are used to float sylvite from halite[85]. Dextrin, starches and certain colloids such as glues, lecithin, casein, and methyl cellulose are mentioned as conditioning agents in combination with cationic promotors[86]. Hydroxyethyl cellulose has been utilized as a collector in a preliminary float designed to remove slime material from a feed to be treated by an amine float[87].

Sylvite also has been concentrated by means of the alcohol sulfates of chain lengths of 5 to 14 carbon atoms[88].

Halite is selectively separated[89] from sylvite by using lead or bismuth salts in combination with cresols, and also fatty acids, and resin acids, as collectors. Alkali resinates; fatty acids and fatty acid soaps (10 or more carbon atoms); naphthenic acids and their alkali metal, ammonium and alkanolamine soaps; cotton seed oils saponified with caustic potash; and cumic acid and its alkali and alkaline earth metal soaps have been recommended as collecting agents in such floats. Frothers such as cresylic acid and the higher alcohols are used in certain of these operations.

Other soluble salts are floated or beneficiated by the flotation method. They include borax and boric acid[90], ammonium chloride from alkali metal nitrates[91], sodium chloride from sodium sulfate[92], and calcium sulfate from sodium chloride[93].

Section 30. *Coal*, both anthracite and bituminous, is floated from ash-forming materials by means of hydrocarbon oils such as fuel oil

in combination with a frother as, for example, pine oil or the higher alcohols. Low ash concentrates are obtained by using 0.5 to 2.0 lb/ton fuel oil and 0.15 to 0.5 lb/ton frothing agent. The quantities of frother used will be observed to be larger than those usually employed in other flotation separations; such quantities are required to obtain a froth which will persist in cleaning flotation to allow the production of concentrates of good grade.

Graphite is similarly floated with a frother-hydrocarbon combination. Pine oil or the higher alcohols are the preferred frothing agents. Common alkaline dispersing agents are also employed.

Sulfur is usually readily floated with a frother-hydrocarbon combination, and concentrates of high grade are obtained where grinding will free the sulfur from the accompanying gangues such as gypsum and silicates. For more intimately associated ores another process involving flotation has been applied[94].

References

1. Gaudin, A. M., "Flotation," McGraw-Hill Book Company, Inc., New York, 1932. (*a*, p. 1; *b*, pp. 54–85; *c*, pp. 1–7).
2. Taggart, A. F., "Handbook of Mineral Dressing," John Wiley & Sons, Inc., New York, 1948. (*a*, sect. 12-01; *b*, 12-02; *c*, 12-03 to 40; *d*, 12-53; *e*, 12-47 to 82; *f*, 12-80).
3. Wark, I. W., "Principles of Flotation," Australasian Institute of Mining and Metallurgy, Melbourne, 1938. (*a*, pp. 21–28 and 45–147; *b*, pp. 15–22; *c*, p. 263).
4. Eguchi, G. M., and Wells, C. H., (to Hawaiian Pineapple Co., Ltd), U. S. Patent 2,518,296 (1950).
   Scott, D. W. (to Ferro Enamel Corp.), U. S. Patent 2,539,486 (1951).
5. Booth, R. B. (to Manville Jenckes Corp.), U. S. Patents 2,153,449 (1939); 2,274,658 and 2,294,827 (1942); Booth, R. B., and Webb, A. M. (to Chemical Construction Corp.), U. S. Patent 2,352,365 (1944); Booth, R. B., and Morash, N. (to American Cyanamid Co.), U. S. Patents 2,436,375 (1948) and 2,578,040 (1951).
6. Elmore, A. S., U. S. Patent 689,070 (1901); Cattermole, A. E., U. S. Patent 777,273 (1904).
7. Delprat, G. D., U. S. Patent 768,035 (1904); Cattermole, A. E., Sulman, H. L., and Kirkpatrick-Picard, H. F., U. S. Patent 788,247 (1905); Sulman, H. L., and Kirkpatrick-Picard, H. F., U. S. Patent 793,808 (1905).
8. Elmore, F. E., U. S. Patent 826,411 (1906).
9. Goyden, G. A., and Laughton, E., U. S. Patent 763,749 (1904).
10. Sulman, H. L., Kirkpatrick, H. F., and Ballot, J., U. S. Patent 835,120 (1906).
11. Sulman, H. L. (to Minerals Separation, Ltd.), U. S. Patent 955,012 (1910); Sulman, H. L., Greenway, H. H., and Higgins, A. H., U. S. Patent 962,678 (1910).

12. Martin, R. B. (to Minerals Separation North American Corp.), U. S. Patent 1,236,857 (1917); Janney, T. A., U. S. Patent 1,491,863 (1924).
13. Perkins, C. L. (to Metals Recovery Co.), U. S. Patents 1,240,597, 1,240,598, and 1,240,599 (1917) 1,302,966 (1919) 1,322,816 (1919) 1,394,639 and 1,394,640 (1921).
14. Sayre, R. E. (to Metals Recovery Co.), U. S. Patent 1,415,899 (1922).
15. Keller, C. H. (to Minerals Separation North American Corp.), U. S. Patent 1,554,216 (1925).
16. Whitworth, F. T., U. S. Patents 1,593,232 (1926) and 2,038,400 (1936).
17. Smith, C. C. (to E. I. du Pont de Nemours & Co.), U. S. Patent 1,652,060 (1927); Bolton, E. K. (to E. I. du Pont de Nemours & Co.), U. S. Patent 1,716,104 (1929).
18. Douglas, W. A. (to E. I. du Pont de Nemours & Co.), U. S. Patent 1,652,099 (1927); Fischer, A. H. (to Guggenheim Brothers), U. S. Patent 1,684,536 (1928).
19. Tveter, E. C. (to The Dow Chemical Co.), U. S. Patent 2,611,485 (1952).
20. Taggart, A. F., Taylor, T. C., and Ince, C. R., *Trans. Am. Inst. Mining Met. Engrs.*, **87** (Milling Methods), 285 (1930).
21. Bates, W. A., and Miller, R. J., *Trans. Am. Inst. Mining Met. Engrs.*, **169,** 385 (1946).
22. Bishop, W. T., *Trans. Am. Inst. Mining Met. Engrs.*, **169,** 379 (1946).
23. Sun, S-C., *Mining Engineering*, **4** (1), 65 (1952).
24. Landolt, G. L., Hill, E. G., and Lowy, A., *Eng. Mining J.*, **129,** 351 (1930).
25. Hansen, M. S. (to Peter C. Reilly), U. S. Patent 1,981,506 (1934).
26. Taggart, A. F., "Handbook of Mineral Dressing," John Wiley & Sons, Inc., New York, 1948. (Sects. 12-45).
27. Greenway, H. H. (to Minerals Separation, Ltd.), U. S. Patent 1,099,699 (1914); McCullough, E. W., and Wilson, R. E. (to Peter C. Reilly), U. S. Patent 1,476,530 (1923); Lewis, C. P. (to Minerals Separation North American Corp.), U. S. Patent 1,560,170 (1925); Klees, A. L. (to Combustion Utilities Corp.), U. S. Patent 1,590,196 (1926).
28. Cunningham, O. D. (to Peter C. Reilly), U. S. Patent 1,925,750 (1933).
29. Christmann, L. J., and Jayne, D. W., Jr. (to American Cyanamid Co.), U. S. Patent 2,250,190 (1941).
30. Sayre, R. E. (to Metals Recovery Co.), U. S. Patent 1,370,366 (1921).
31. Sayre, R. E. (to Metals Recovery Co.), U. S. Patent 1,378,562 (1921); Herrly, C. J. (to Carbide and Carbon Chemicals Corp.), U. S. Patent 1,549.833 (1925).
32. Patek, J. M., U. S. Patent 2,000,350 (1935).
33. Sayre, R. E. (to Metals Recovery Co.), U. S. Patent 1,370,843 (1921).
34. Woodhouse, J. E. (to E. I. du Pont de Nemours & Co.), U. S. Patent 2,251,217 (1941).
35. Bishop, W. T., Lorand, E. J., and Reese, J. E. (to Hercules Powder Co.), U. S. Patent 2,467,369 (1949).
36. Bishop, W. T., Lorand, E. J., and Reese, J. E. (to Hercules Powder Co.), U. S. Patent 2,535,344 and 2,535,345 (1950).
37. Bishop, W. T., Lorand, E. J., and Reese, J. E. (to Hercules Powder Co.), U. S. Patent 2,545,132 (1951).

38. Lorand, E. J., and Reese, John E. (to Hercules Powder Co.), U. S. Patent 2,548,435 (1951).
39. Potgieter van Aardt, J. H. (to R. F. Powell and National Chemical Products Co.), U. S. Patent 2,561,251 (1951).
40. Powell, R. F., and Stanley, H. M., U. S. Patent 2,591,289 (1952).
41. Frederick, H. E. (to W. H. Bissel, F. S. Simmicks, G. J. Herry), U. S. Patent 1,438,435 and 1,438,436 (1922), 1,490,736 (1924).
42. Bates, W. A. (to California Research Corp.), U. S. Patent 2,594,612 (1952).
43. Bishop, W. T. (to Hercules Powder Co.), U. S. Patent 2,446,207 (1948).
44. Ruth, J. P., Jr., U. S. Patent 1,356,832 (1920).
45. Perkins, C. L., and Sayre, R. E. (to Metals Recovery Co.), U. S. Patent 1,370,357 (1921).
46. Stevens, J. L., U. S. Patent 1,614,089 (1927).
47. Kirby, J. E., and Werntz, J. H. (to E. I. duPont de Nemours & Co.), U. S. Patent 2,099,120 (1937).
48. Ralston, A. W., and Pool, W. O. (to Armour and Co.), U. S. Patent 2,175,093 (1939).
49. Ralston, A. W., Pool, W. O., and Harwood, J. (to Armour and Co.), U. S Patent 2,185,968 (1940).
50. Christmann, L. J., and Jayne, D. W., Jr. (to American Cyanamid Co.), U. S. Patent 2,065,053 (1936).
51. Cannon, H., Barbre, C., and Leslie, E. H. (to General Petroleum Corp.), U. S. Patent 1,337,542 (1920); Rhodes, F. H. (to the Barrett Co.), U. S. Patent 1,506,385 (1924); Tunison, B. R., U. S. Patents 1,677,416 (1928) and 1,709,447 (1929).
52. Clevenger, G. H., U. S. Patent 1,212,130 (1917).
53. Wilkerson, E. W. (to Minerals Separation North American Corp.), U. S. Patents 1,398,989 and 1,398,990 (1921)
54. Luckenbach, R. (to Luckenbach Processes, Inc.), U. S. Patent 1,425,327 (1922).
55. Forrest, C. N. (to Barber Asphalt Paving Co.), U. S. Patent 1,438,590 (1922).
56. James, J. H. (to C. P. Byrnes), U. S. Patents 1,439,107 (1922) and 1,549,316 (1925); Eisele, J., Griessbach, R., and Heuck, C. (to I. G. Farbenindustrie Aktiengesellschaft), U. S. Patent 1,787,938 (1931).
57. Adams, G. L. (to Standard Oil Development Co.), U. S. Patents 1,678,311 and 1,678,312 (1928).
58. Yaryan, H. T., U. S. Patent 1,191,053 (1916); Luckenbach, R. (to Luckenbach Processes, Inc.), U. S. Patents 1,386,716 (1921) 1,417,261, 1,417,262, and 1,417,263 (1922) 1,448,929, 1,457,708, and 1,473,192 (1923); Schwarz, A (to Metals Recovery Co.), U. S. Patent 1,427,232 (1922); Luckenbach, R., U. S. Patent 1,722,528 (1929).
59. Nagel, K. (to Deutsche Gold- und Silber-Scheideanstalt vormals Roessler), U. S. Patent 2,148,275 (1939).
60. Edser, E., and Tucker, S. (to Minerals Separation North American Corp.), U. S. Patent 1,337,548 (1920); Patterson, D. W., and Woolfenden, H. L., U. S. Patent 1,412,215 (1922); Sulman, H. L., and Edser, E. (to Minerals Separation North American Corp.), U. S. Patent 1,492,904 (1924); Carua

han, T. S. (to Union Minière Du Haut Katanga Société Congolaise), U. S. Patent 1,671,698 (1928); Luckenbach, R., U. S. Patent 1,688,975 (1928); Hasselstrom, T., U. S. Patents 1,986,816 and 1,986,817 (1935); Hodges, P. (to Gulf States Paper Co.), U. S. Patent 1,992,949 (1935); Weed, F., and Ellis, E. E., U. S. Patent 2,014,406 (1935); Ralston, A. W., and Pool, W. O. (to Armour and Co.), U. S. Patent 2,122,659 (1938); Ralston, A. W., and Pool, W. O. (to Armour and Co.), U. S. Patent 2,125,852 (1938); Ralston, A. W., and Pool, W. O. (to Armour and Co.), U. S. Patent 2,149,546 (1939); Handy, R. S., U. S. Patent 2,164,063 (1939); Hills, R. C. (to Freeport Sulphur Co.), U. S. Patent 2,259,420 (1941).

61 Higgins, A. H. (to Minerals Separation American Syndicate [1913], Ltd.), U. S. Patent 1,170,637 (1916); Quigley, C. G., U. S. Patents 1,771,550 and 1,773,787 (1930); Lutz, G. (to Grasselli Chemical Co.), U. S. Patent 1,765,308 (1930); Lenher, S. (to E. I. du Pont de Nemours & Co.), U. S. Patent 2,012,609 (1935); Lenher, S., Gillson, J. L., and Mentzer, C. T. (to E. I. du Pont de Nemours & Co.), U. S. Patent 2,074,699 (1937); Gillson, J. L., and Mentzer, C. T. (to E. I. du Pont de Nemours & Co.), U. S. Patent 2,112,362 (1938); Lenher, S., and Gillson, J. L. (to E. I. du Pont de Nemours & Co.), U. S. Patent 2,116,727 (1938); Harris, B. R., U. S. Patent 2,120,217 (1938); Epstein, A. K., and Katzman, M. (to The Emulsol Corp.), U. S. Patent 2,178,139 (1939); Katzman, M. B. (to The Emulsol Corp.), U. S. Patent 2,184,770 (1939); Harris, B. R., U. S. Patent 2,194,522 (1940); Gaylor, P. J. (to Standard Oil Development Co.), U. S. Patent 2,230,565 (1941); Phelps, D. S. (to Edgar Brothers Co.), U. S. Patent 2,249,569 (1941); Lane, G. J., and Phelps, D. S. (to Edgar Brothers Co.), U. S. Patent 2,249,570 (1941); Coke, H. W., U. S. Patent 2,285,394 (1942); Ray, P. A. (to Hercules Powder Co.), U. S. Patent 2,286,374 (1942); see also reference 75.

62. Callow, J. M. (to Metals Recovery Co.), U. S. Patent 1,141,377 (1915).

63. Anonymous Article: *Eng. and Mining J.*, **122,** 874 (1926).

64. Forrester, D. W., U. S. Patent 1,646,019 (1925).

65. Taggart, A. F., "Handbook of Mineral Dressing," John Wiley & Sons, Inc., New York, 1948. (*a*, sect. 12-71; *b*, 12-70; *c*, 12-68; *d*, 12-64; *e*, 12-66).

66. Breerwood, C. H., and Williams, J. C. (to Separation Process Co.), U. S. Patents 2,161,010 and 2,161,011 (1939); Reid, R. C. (to Separation Process Co.), U. S. Patents 2,163,701 and 2,163,702 (1939); Vogel-Jorgensen, M. (to Separation Process Co.), U. S. Patent 2,165,268 (1939); Reid, R. C. (to Separation Process Co.), U. S. Patent 2,202,601 (1940); Weinig, A. J. (to Riverside Cement Co.), U. S. Patent 2,208,143 (1940); Vogel-Jorgensen, M. (to Separation Process Co.), U. S. Patent 2,216,992 (1940); Vogel-Jorgeusen, M. (to Separation Process Co.), U. S. Patent 2,255,139 (1941); Christmann, L. J., and Erickson, S. E. (to American Cyanamid Co.), U. S. Patent 2,335,485 (1943); Jayne, D. W., Jr., Erickson, S. E., and Day, H. M. (to American Cyanamid Co.), U. S. Patent 2,336,014 (1943); Heilman, T. (to Separation Process Co.), U. S. Patent 2,349,094 (1944); Heilman, T. (to Separation Process Co.), U. S. Patents 2,507,012 and 2,507,013 (1950); Vogel-Jorgensen, M. (to Separation Process Co.), U. S. Patent 2,526,519 (1950).

67. Doerner, H. A., and Harris, D. L. (to State College of Washington Research Foundation), U. S. Patent 2,205,293 (1940); Fahrenwald, A. W. (to Northwest Magnesite Co.), U. S. Patent 2,280,905 (1942); Weinig, A. J. (to Basic Magnesium, Inc.), U. S. Patents 2,363,029, 2,363,030, and 2,363,031 (1944); Lafforge, J. W., U. S. Patent 2,373,123 (1944); Woodward, H. S., and Bates, W. A. (to Defense Plant Corp.), U. S. Patent 2,393,008 (1946).
68. Broadbridge, W., and Edser, E. (to Minerals Separation North American Corp.), U. S. Patent 1,547,732 (1925); Trotter, W., and Wilkinson, E. W. (to Minerals Separation North American Corp.), U. S. Patent 1,761,546 (1930); Trotter, W., and Wilkinson, E. W. (to Minerals Separation North American Corp.), U. S. Patent 1,795,100 (1931); Johnston, F. F. (to Phosphate Recovery Co.), U. S. Patent 1,927,939 (1933); Siems, H. B. (to Swift & Co. Fertilizer Works), U. S. Patent 2,084,413 (1937); Christmann, L. J. (to American Cyanamid Co.), U. S. Patent 2,300,827 (1942); Greene, E. W., and Head, C. W. (to Phosphate Recovery Corp.), U. S. Patent 2,303,931 (1942); Erickson, S. E., and Jayne, D. W., Jr. (to American Cyanamid Co.), U. S. Patent 2,312,466 (1943); Christmann, L. J., and Erickson, S. E. (to American Cyanamid Co.), U. S. Patent 2,377,129 (1945); Gieseke, E. W. (to American Cyanamid Co.), U. S. Patent 2,466,671 (1949).
69. Crago, A. (to Phosphate Recovery Corp.), U. S. Patent 2,293,640 (1942).
70. Harwood, J., and Pool, W. O. (to Armour and Co.), U. S. Patent 2,166,093 (1939); Ralston, A. W., and Pool, W. O. (to Armour and Co.), U. S. Patent 2,168,849 (1939); Kritchevsky, W. (to Ninol, Inc.) U. S. Patent 2,192,644 (1940); Trotter, W., and Wilkinson, E. W. (to Minerals Separation North American Corp.), U. S. Patent 2,205,503 (1940); Christmann, L. J., Jayne, D. W., Jr., and Erickson, S. E. (to American Cyanamid Co.), U. S. Patent 2,278,060 (1942); Jayne, D. W., Jr., Erickson, S. E., and Day, H. M. (to American Cyanamid Co.), U. S. Patent 2,278,107 (1942); Erickson, S. E. (to American Cyanamid Co.), U. S. Patent 2,295,459 (1942); Corley, H. M., Anderson, A. W., and Segebrecht, E. W. (to Armour and Co.), U. S. Patent 2,298,281 (1942); Katzman, M., and Harris, B. R. (to The Emulsol Corp.), U. S. Patent 2,299,756 (1942); Greene, E. W. (to Phosphate Recovery Corp.), U. S. Patent 2,299,893 (1942); Christmann, L. J., Jayne, D. W., Jr., and Erickson, S. E. (to American Cyanamid Co.), U. S. Patent 2,312,387 (1943); Jayne, D. W., Jr., Erickson, S. E., and Day, H. M. (to American Cyanamid Co.), U. S. Patent 2,312,414 (1943); Ralston, A. W., and Segebrecht, E. W. (to Armour and Co.), U. S. Patent 2,313,360 (1943); Christmann, L. J., Jayne, D. W., Jr., and Erickson, S. E. (to American Cyanamid Co.), U. S. Patent 2,321,186 (1943); Jayne, D. W., Jr., Day, H. M., and Gieseke, E. W. (to American Cyanamid Co.), U. S. Patent 2,336,015 (1943); Erickson, S. E. (to American Cyanamid Co.), U. S. Patent 2,336,437 (1943); Jayne, D. W., Day, H. M., and Erickson, S. E. (to American Cyanamid Co.), U. S. Patent 2,336,868 (1943); Lontz, J. F. (to E. I. du Pont de Nemours & Co.), U. S. Patent 2,337,118 (1943); Maust, E. J., and Hollingsworth, C. A. (to American Cyanamid Co.), U. S. Patent 2,343,221 (1944); Jayne, D. W., Day, H. M., and Erickson, S. E. (to American Cyanamid Co.), U. S. Patent 2,362,276 (1944); Cahn, F. J. (to The Emulsol Corp.), U. S. Patent

2,362,432 (1944); Christmann, L. J., Jayne, D. W., Jr., and Erickson, S. E. (to American Cyanamid Co.), U. S. Patent 2,364,272 (1944); Jayne, D. W., Jr., Day, H. M., and Gieseke, E. W. (to American Cyanamid Co.), U. S. Patent 2,365,084 (1944); Christmann, L. J. (to American Cyanamid Co.), U. S. Patent 2,368,968 (1945); Jayne, D. W., Jr., Day, H. M., and Gieseke, E. W. (to American Cyanamid Co.), U. S. Patent 2,380,698 (1945); Schilling, K. F., Cole, A. T., Duke, J. B., and Houston, W. M. (to Minerals Separation North American Corp.), U. S. Patent 2,382,178 (1945); Cahn, F. J. (to The Emulsol Corp.), U. S. Patent 2,389,763 (1945); Schilling, K. F. (to Minerals Separation North American Corp.), U. S. Patent 2,400,213 (1946); Schilling, K. F. (to Minerals Separation North American Corp.), U. S. Patents 2,459,966 and 2,459,967 (1949); Duke, J. B. (to Minerals Separation North American Corp.), U. S. Patent 2,461,813 (1949); Jayne, D. W., Day, H. M., and Gieseke, E. W. (to American Cyanamid Co.), U. S. Patent 2,494,132 (1950); Evans, R. D. (to American Agricultural Chemical Co.), U. S. Patent 2,553,905 (1951); Jayne, D. W., Day, H. M., and Gieseke, E. W. (to American Cyanamid Co.), U. S. Patent 2,569,417 (1951).

71. Clemmer, J. B., and Anderson, C. O. (to Mahoning Mining Co.), U. S. Patent 2,168,762 (1939); Williams, J. C., and Greeman, O. W. (to Aluminum Company of America), U. S. Patent 1,785,992 (1930); Duncan, W. E. (to Mahoning Mining Co.), U. S. Patent 2,381,120 (1945); Clemmer, J. B., and Clemmons, B. H. (to United States of America as represented by the Secretary of Interior), U. S. Patent 2,407,651 (1946).
72. Borcherdt, W. O. (to New Jersey Zinc Co.), U. S. Patents 1,662,633 and 1,662,634 (1928); Hoag, E. H., U. S. Patents 2,371,292 and 2,378,552 (1945); Gieseke, E. W. (to American Cyanamid Co.), U. S. Patent 2,483,970 (1949).
73. Gieseke, E. W. (to American Cyanamid Co.), U. S. Patent 2,373,305 (1945); Burwell, B., and Brennan, J. H. (to U. S. Vanadium Corp.), U. S. Patent 2,459,868 (1949).
74. DeVaney, F. D. (to Erie Mining Co.), U. S. Patent 2,470,150 (1949).
75. Booth, R. B., and Herkenhoff, E. C. (to American Cyanamid Co.), U. S. Patents 2,385,054 (1945) 2,410,376 and 2,410,377 (1946) 2,414,714 and 2,433,258 (1947) 2,439,200 (1948) 2,461,875 and 2,475,581 (1949); Bates, W. A. (to California Research Corp.), U. S. Patent 2,547,148 (1951); Barr, J. A. (to Armour and Co.), U. S. Patent 2,607,486 (1952).
76. Brown, E. H., and Tartaron, F. X. (to Minerals Separation North American Corp.), U. S. Patents 2,364,618, 2,364,777, and 2,364,778 (1944); Clemmer, J. B., and Clemmons, B. H. (to United States of America as represented by the Secretary of the Interior), U. S. Patent 2,383,467 (1945); Clemmer, J. B., and Rampacek, C. (to United States of America as represented by the Secretary of the Interior), U. S. Patent 2,403,481 (1946); Clemmer, J. B., and Williams, M. F. (to United States of America as represented by the Secretary of the Interior), U. S. Patent 2,415,416 (1947); Clemmer, J. B., and Williams, M. F., U. S. Patent 2,419,945 (1947); Herkenhoff, E. C. (to American Cyanamid Co.), U. S. Patent 2,423,022 (1947); Herkenhoff, E. C. (to American Cyanamid Co.), U. S. Patent 2,496,050 (1950);

Morton, R. J. (to Oliver Iron Mining Co.), U. S. Patent 2,551,893 (1951); Sullivan, W. L. (to Minerals Separation North American Corp.), U. S. Patent 2,555,825 (1951).

77. DeVaney, F. D. (to Erie Mining Co.), U. S. Patents 2,388,471 (1945) 2,410,021 (1946) 2,450,720 (1948) 2,483,890 (1949).

78. Booth, R. B., and Pickens, R. A. (to American Cyanamid Co.), U. S. Patents 2,428,763 (1947) and 2,477,402 (1949).

79. Tartaron, F. X. (to Phosphate Recovery Corp.), U. S. Patents 2,289,141 and 2,305,502 (1942); Tartaron, F. X. (to Minerals Separation North American Corp.), U. S. Patent 2,326,807 (1943).

80. Pickens, R. A. (to American Cyanamid Co.), U. S. Patent 2,387,856 (1945); McMurray, L. L. (to American Cyanamid Co.), U. S. Patent 2,466,995 (1949); Moyer, S. P. (to American Cyanamid Co.), U. S. Patent 2,471,341 (1949); Moyer, S. P. (to American Cyanamid Co.), U. S. Patent 2,494,139 (1950); McMurray, L. L., and Moyer, S. P. (to American Cyanamid Co.), U. S. Patent 2,525,146 (1950); Moyer, S. P. (to American Cyanamid Co.), U. S. Patent 2,557,455 (1951).

81. O'Meara, R. G. (to Government of the U. S. as represented by the Secretary of the Interior), U. S. Patent 2,297,689 (1942).

82. Phelps, D. S. (to Edgar Plastic Kaolin Co.), U. S. Patent 2,257,808 (1941); Tartaron, F. X., and Cole, Allen T. (to Phosphate Recovery Co.), U. S. Patent 2,283,295 (1942); Tartaron, F. X., and Cole, Allen T. (to Phosphate Recovery Co.), U. S. Patent 2,303,962 (1942); Duke, J. B. (to Minerals Separation North American Corp.), U. S. Patent 2,459,219 (1949).

83. Harris, B. R., U. S. Patent 2,177,985 (1939); Cole, A. T. (to Minerals Separation North American Corp.), U. S. Patent 2,340,580 (1944); Cole, A. T., Duke, J. B., and McMurray, L. L. (to Minerals Separation North American Corp.), U. S. Patent 2,409,665 (1946); Stokes, E. B. (to Minerals Separation North American Corp.), U. S. Patent 2,433,633 (1947).

84. Gieseke, E. W. (to American Cyanamid Co.), U. S. Patent 2,483,192 (1949); Lenhart, W. B., *Rock Products*, **55**, 100 (1952).

85. Kirby, J. E. (to E. I. du Pont de Nemours & Co.), U. S. Patent 2,088,325 (1937); Weiner, N. (to Bonneville, Ltd.), U. S. Patents 2,329,149 (1943) and 2,382,360 (1945); Schilling, K. F., Cole, A. T., and Houston, W. M. (to Minerals Separation North American Corp.), U. S. Patent 2,382,178 (1945); Greene, E. W., Sherertz, J. R., and Cole, A. T. (to Minerals Separation North American Corp.), U. S. Patent 2,420,476 (1947); Schilling, K. F. (to Minerals Separation North American Corp.), U. S. Patents 2,459,966 and 2,459,967 (1949); Weinig, A. J. (to Potash Company of America), U. S. Patent 2,588,443 (1952).

86. Cole, A. T., Duke, J. B., and Schilling, K. F. (to Minerals Separation North American Corp.), U. S. Patent 2,322,789 (1943); Cole, A. T. (to Minerals Separation North American Corp.), U. S. Patent 2,365,805 (1944); Cole, A. T., and Houston, W. M. (to Minerals Separation North American Corp.), U. S. Patent 2,364,520 (1944).

87. Jackson, R. I. (to International Minerals & Chemical Corp.), U. S. Patent 2,569,672 (1951).

88. Harris, B. J., U. S. Patent 2,182,845 (1939); Weinig, A. J. (to Potash Company of America), U. S. Patents 2,188,931 (1940) and 2,349,393 (1944).
89. Weinig, A. J. (to Potash Company of America), U. S. Patents 2,188,933 (1940) 2,211,396 and 2,211,397 (1940); Anderson, L. D. (to Potash Company of America), U. S. Patent Reissue 21,566 (1940); Weinig, A. J. (to Potash Company of America), U. S. Patents 2,222,330, 2,222,331, and 2,222,332 (1940); Ray, P. A. (to Hercules Powder Co.), U. S. Patent 2,389,080 (1945).
90. Campbell, T. P., and Jacobsen, W. B., U. S. Patent 2,175,178 (1939); Malozemoff, P., MacAfee, M. W., and Kirk, Miles W. (to Pacific Coast Borax Co.), U. S. Patent 2,184,558 (1939); Shelton, K. F. (to Government of U. S. as represented by the Secretary of the Interior), U. S. Patent 2,317,413 (1943); Pearson, E. P. (to American Potash and Chemical Corp.) U. S. Patent 2,333,334 (1943).
91. Dessèvre, J., U. S. Patent 2,189,488 (1940).
92. Pye, D. J. (to The Dow Chemical Co.), U. S. Patent 2,310,315 (1943).
93. Perkins, E. C. (to E. I. du Pont de Nemours & Co.), U. S. Patent 2,340,613 (1944).
94. McGauley, P. J., Roberts, E. S., and Strelzoff, S. (to Chemical Construction Corp.), U. S. Patent 2,537,842 (1951).
95. Christmann, L. J. (to American Cyanamid Co.), U. S. Patent 1,866,296 (1932).
96. Wrobel, S. A., "Flotation Frothers," *Chem. Trade J. (London)*, **131**, 824 (1952).
97. Christensen, N. C., U. S. Patent 1,467,354 (1923); Lenher, S. (to E. I. du Pont de Nemours & Co.), U. S. Patent 2,132,902 (1938).
98. McKenna, W. J., Lessels, V., and Peterson, E. C. (to International Smelting and Refining Co.), U. S. Patent 2,482,859 (1949).

14. MISCELLANEOUS USES OF FOAM

Section 1. The oldest utilization of foam originated probably before the human race. There are several insects (so-called spittle insects) which protect themselves by froth. The froghopper (belonging to the genus *Philaenus*, *Cercopidae*) is the best known instance. The nymph of this species, after the hatching from the egg, secretes a froth whose volume is many times that of the insect and then lives under this froth for several weeks. The froth is not destroyed by rain or by direct sun rays. Apparently neither the physical nor the chemical properties of this "cuckoo spit" have been investigated, and the mechanism of froth formation by the nymph also seems to be still in doubt; some authorities believe the foam to be of pneumatic origin while others say it is produced by whipping. No data could be found on the kind of protection afforded by the "spittle."

Section 2. Uses of foam by man can generally be classified according to the property utilized, although in some instances the advantages of foam application are not at all evident and in others more than one property is turned to account. In this chapter the material is presented in the following order:

(a) Foams used for immobilizing gas or liquid
(b) Foams used because of their great volume or great interface
(c) Solid foams
(d) Separation of suspended or dissolved matter by foam
(e) Foams used for measurement or analysis.

Foams Used for Immobilizing Gas or Liquid

Section 3. Fire-fighting foams belong to this group but are discussed separately (Chapter 12) because of their importance.

In fighting gasoline fires foam hinders mixing of gasoline vapor with air. Free access of vapor to air is necessary also for evaporation of gasoline. Hence, this evaporation may be retarded by covering gasoline with a froth of air or carbon dioxide in an emulsion of soap, water, and kerosene[1].

Fluxes used in galvanizing often contain frothers. The froth on the

surface of molten zinc is supposed to retard decomposition of the flux (usually ammonium chloride) and to reduce spattering of the liquid. As frothers, bran, sawdust, tallow, and similar organic materials are employed. Pentaerythrol is claimed to give stable froth (e.g., 40 cm thick) without unduly contaminating the flux[2].

Insecticide gases can be blown away, and insecticide liquids run down to the ground. When gas and liquid are mixed to a foam, they remain for long attached to the foliage which has to be freed from insects. Thus, plants are sprayed with foams produced by dissolving calcium cyanide in water containing saponin and dispersing air in the solution[3] (see also ref. 4).

Froth can also be made by mixing two suitable salves at the place of application. Thus the insecticidal nicotine sulfate can be incorporated in a foam which forms when sodium carbonate or bicarbonate is mixed with tartaric acid or aluminum acetate, both components being distributed in a mixture of gum tragacanth and aqueous glycerol[5]. Application of insecticidal foam to human skin also was claimed[6]. Foam formation occurs when the preparation warms up in contact with the skin. The frother in these preparations is gelatin, and the gas is liberated in a reaction between tartaric acid or aluminum sulfate with sodium carbonate or sodium bicarbonate, or between tartaric acid and sodium sulfide, or between hydroxylamine hydrochloride and sodium nitrite.

Substances used for decontaminating areas subjected to poison gas attack can be immobilized in a foam. Thus, oxidizing salts such as NaClO, $NaClO_2$, or CaCl(OCl) are dissolved in water containing soap or a synthetic detergent, the solution is transformed into foam, and this is spread over the contaminated surface[7].

Foams Used Because of Their Great Volume or Great Interface

Section 4. Exchange of matter between a liquid and a gas phase should generally be accelerated when the liquid-gas interface is made as extensive as it is in foam.

Luchinskii[8, 9] noticed that foams rapidly absorb gases whose absorption by liquids is very slow. Thus nitrogen oxides are sluggishly taken up even by liquids chemically reacting with these oxides, such as solutions of hydrogen peroxide, potassium iodide, etc. Foams intercept also aerosols which, as a rule, do not lose any of their suspended contents on bubbling through a liquid. Presumably the difference in

the behavior between a bubble in froth and a similar bubble in liquid is due above all to the small speed of ascent of foam bubbles. A bubble spends so much time in froth that the particles suspended in it have opportunity to settle, i.e., to reach the liquid phase. Suppose, for example, that the froth is stable for one minute and that the cells in it are 1 mm across. Bubbles of 1 mm in diameter would rise in water about 100 meters in one minute; thus a layer of froth is equivalent to a much heavier layer, about 100 meters thick, of water. Contact of aerosol particles with the liquid walls is accelerated also by agitation of the gas phase. This agitation occurs when bubbles burst and is promoted also by periodic variation of the linear velocity of the aerosol, achieved by passing the froth through a column whose cross section periodically changes along its length.

Foam was suggested for absorption of sulfuric acid mist contained in the fumes expelled in the process of concentration of sulfuric acid[10]. "Green acid," i.e., the sludge obtained in the customary treatment of petroleum oils with concentrated sulfuric acid, was the frothing agent. Mists containing 1 to 3 mg/l of sulfuric acid had to spend at least 10 sec. in the froth to lose 90 per cent of their acid content. When the contact time was 12 sec. or more, removal of over 90 per cent was achieved also for more concentrated mists (of about 30 mg/l). The foaming capacity of solutions of "green acid" was very sensitive to contamination with iron; as little as 0.05 per cent Fe markedly reduced the foam stability.

Sewage is purified by bubbling air through it. This is a well established procedure described in books and articles. However, it has apparently not been investigated how far the degree of purification achieved depends on the presence (or absence) of foam above the aeration tank[11].

Drying and degassing of oils in a vacuum are accelerated by adding frothers to the oil. The foam produced had a large liquid-gas interface, and gases escape from the liquid more rapidly[12].

Foam was used for bleaching and dyeing textiles. For instance, foam, whose gas phase consisted of chlorine (for bleaching) or whose liquid phase was a dye solution, was forced through a single layer of fabric or through a garment[13]. Compared with the usual methods of application this procedure was claimed to result in greater uniformity of spread, enhanced penetration of the active agent into the material, decreased time of treatment, and in less damage to the goods because of handling. The collapsed foam was again mixed with gas and used

for subsequent treatment. In another method[14] the fabric to be dyed (cotton) was placed in the foam produced by boiling. Superheated steam passed through coils submerged in a coloring solution (of a substantive or a sulfur dye) containing also a sulfonated oil or sulfonated alcohol as frothing agent. The dyeing occurred in the foam of this solution. This procedure required no movable parts in the apparatus.

Foam is said to transport drugs to otherwise inaccessible parts of body cavities and to ensure longer contact between the drug and the cavity walls[15]. Frothing is achieved by mixing jellies *A* and *B*. *A* is prepared by alkaline treatment (e.g., with sodium carbonate or sodium orthophosphate) of gum karaya. *B* is made by the same alkaline treatment followed by acidification (e.g., with glyceroboric acid). *A* contains a carbonate, and carbon dioxide evolved on mixing *A* and *B* is the gas phase of the froth while the liquid phase contains the drug required.

It is known that thin adhesive joints are stronger than thick ones. However, application of a small amount of adhesive may result in bare patches on the surface of the solids to be glued together. Foams which have great volume and little substance ensure uniform coverage of solid surfaces with a small amount of adhesive[16]. For instance, 100 parts of aqueous melamine–formaldehyde glue are agitated with 1 part saponin, 1 part ammonium chloride (as "foam hardener"), and 8 parts water until the volume is about doubled. As an adhesive, one volume of this froth can be substituted for one volume of the original glue thus effecting saving of about 50 per cent. The foam is stable for 3 or 4 days and is not destroyed by raising the temperature to 100°. A special agitator for producing adhesive foams has been built[17].

In pyrotechnics the striking expansion accompanying foam formation is used in "black nonmercury snakes"[18]. They consist, for example, of picric acid, which yields a large volume of gas on ignition, and pitch (plasticized with linseed oil) which supplies the material of the foam films.

Match heads contain a solid foam of glue. Incorporation of air permits slow, even burning. When the match head is too dense, the match pops, sputters, or explodes when struck[19].

Solid Foams

Section 5. Solid foams in this chapter are not classified according to the property utilized, as being a foam usually confers more than

one advantage. In many instances sponges can do as much as do solid foams, and there are many materials which are partly sponge and partly foam and also materials which are sponges but are called foams. In a foam, be its films liquid or solid, they fully separate each bubble from all its neighbors, while in a sponge the bubbles communicate with each other and both solid and gas are continuous phases.

Section 6. Bread is the most important solid foam (or partly foam, partly sponge). Undoubtedly, bread is preferred to nonporous food of the same chemical composition (and food value) because of its large solid-gas interface which accelerates the action of digestive juices on it. The ancient art of bread-making is not fundamentally different from the most modern procedures of the manufacture of multicellular goods. Gas (e.g., carbon dioxide from yeast) is liberated in a mass (dough) which is still plastic; then the bubble walls are hardened by heat, and a relatively rigid foam results.

Many other familiar foods are solid foams, e.g., "angel cake"[20]. Certain oriental sweets are said to contain saponin in the form of soaproot. Saponins are not harmless substances, and not more than 2 parts saponin should be used for 1,000 parts of food[21]. Commercial glyceryl monostearate is used in the food industry as a whipping agent; it is a mixture of glyceryl monostearates and monopalmitates with small amounts of diesters and triesters of glycerol[22].

Whipping agents for food can be prepared by condensing sorbitan monostearate with 4 to 20 molecules of ethylene oxide. According to the amount of ethylene oxide employed the condensation products are more water-soluble or more oil-soluble, and mixtures of two different products proved to be better frothers than single compounds[23].

Proteins are popular frothing agents in the food industry. Casein and some other proteins become powerful frothers after partial degradation. For example, 5 parts of casein are mixed with 1 part of calcium hydroxide and 8 parts of water, and the mixture is kept for several days until its pH decreases from about 12 to about 10 or until its polypeptide content increases to 20–25 per cent. The product is a satisfactory substitute for egg white (as far as foaming properties are concerned) in ice cream and confectionery products[24]. Whey yields a frother when lactose and acid-insoluble ingredients are removed from it[25].

Soybean proteins and their degradation products are used as foaming agents in food also, as in fire-fighting foams (Chapter 12). For example, the protein is partly digested with pepsin and hydrochloric acid, and then calcium hydroxide is added to pH 8; calcium seems to increase the duration of polypeptide foams[24]. In another procedure first glycinin (which is the main protein of soya) is isolated in relatively pure state and then digested with pepsin and hydrochloric acid until the percentage of nonprotein nitrogen reaches 20 to 35 per cent[26] or 15 to 30 per cent[27]. The quality of the foam obtained from the last mentioned procedure was tested by measuring the rate of drainage. The degraded glycinin served as frother in nougats, fudge, and so on.

Section 7. "Foamglass" (and the materials of construction discussed in section 8) combines the advantages of light weight (i.e., large volume) and good insulating properties for heat and sound. Their efficiency as heat insulators is due to the immobilization of gas in them, i.e., to the absence of connection between the neighboring bubbles; this structure eliminates convection which so often is the main component of heat transfer.

In the manufacture of transparent glass the glass melt, after the completion of the chemical reaction of glass formation, is "fined," i.e., kept at a temperature high enough for the glass to be freely flowing; during this stage gas bubbles present in the melt rise to its surface and escape. In the manufacture of glass foam the melt contains very many bubbles (e.g., because the original batch contained gas-involving ingredients) and is kept at a temperature so low that bubbles do not rise but only slowly expand in the highly viscous medium[28].

Many modifications of this procedure are possible. For instance, instead of the direct change from melting to softening temperature, the melt may first be cooled until rigid and then heated again to the softening temperature[28]. This manufacture in two steps has the advantage that the second step can be carried out at another time and place than the first step. Thus the second step may be accomplished in a mold. When cold glass containing bubbles is introduced into the mold (without filling it) and is then heated to and kept in the softening range, the bubbles expand and the mass fills the mold thus acquiring the prescribed shape[28]. The expansion can be assisted by

application of a vacuum[28, 29]. In another modification of the process[29, 30], powder of ordinary glass is mixed with a powder capable of liberating gas at high temperature and then heated to a temperature "at which the glass particles become soft and are joined one to the other simply by contact." This temperature range may be, for example, 200° above the softening range, and the product obtained is claimed to be more uniform than that prepared by the earlier methods. This seems to be the method mainly employed in industry[31]; crushed glass and a "very small amount" of pure carbon are ground together "to a powder much finer than talcum" and then heated in a mold. Crushed glass can be heated also without any addition of a gas-liberating substance; then air and water occluded in the powder act as sources of the gas phase in the bubbles[32]. A continuous process of manufacturing vesicular glass consists in the introduction of a gas into molten glass and then "drawing forth the froth from the top of the mass as a continuous sheet"[33].

The gas phase of glass foam may consist of air and water vapor, as in ref. 30 and 32. The amount of air and water available may be increased by adding to crushed glass either kieselguhr as this contains much adsorbed moisture and air, or a hydrated salt (such as hydrated magnesium silicate)[30]. If gas is produced from sodium sulfate and charcoal, it consists mainly of sulfur dioxide[30]. Best results are claimed when the batch contains 0.5 per cent finely divided carbon and 0.1 to 0.2 per cent calcium sulfate hemihydrate[34].

The bubbles in glass foam are about 0.05 to 0.5 cm large[35]. The density is between 0.15 and 0.50 g/cm^3 (solid glasses usually have densities near 2.5)[35]; the usual value is 0.16 (= 10 lb/cu ft)[31]. According to Sanders, commercial foam glass has compressive strength of 11 bars (150 lb/sq in.) while Kreidl gives the value of 40 bars. Modulus of rupture (flexural strength) is 9 bars (130 lb/sq in.), tensile strength 6 bars (84 lb/sq in.), shear strength 4.5 bars (64 lb/sq in.), modulus of elasticity 15 kilobars (200,000 lb/sq in.), impact strength 10^9 ergs (66 ft-lb), and heat conductivity at 10° 0.00009 cal./cm sec. °C (0.40 Btu/hr sq ft °F/in.). The corresponding constants of foam glass manufactured in Russia can be found in ref. 35a.

Foam glass has the great advantage that it can be shaped almost as easily as wood. It can be sawed, cut, drilled, and so on.

Section 8. Of the other "multicellular" building materials some are solid foams and some are sponges or mats. However all the fol-

lowing materials (in this section) at least pass through the stage of foam. For instance, sand, portland cement, and aluminum caseinate suspended in water are whipped to a foam; when this foam sets, a light-weight cellular concrete is obtained[36].

Many other frothers have been recommended instead of aluminum caseinate. They include rosin + gelatin + formaldehyde, phenol + gelatin + formaldehyde + saponin, soap bark[37], soap bark extract + karaya gum[38], esters of polyphosphoric acids[39], and so on.

Light gypsum tile or light "wallboard having paper sheet liners from calcined gypsum and water" can be obtained if the aqueous gypsum suspension is foamed before it sets[40]. As frothers, gelatinized starch and soap bark[40] or rosin size and alkali caseinate[41] can be used.

Sulfite liquor acts as a frothing agent in the production of porous board[42].

Foamed slag, used for structural light-weight concrete and presumably similar in its structure to foam glass, can be made, for example, by injecting water into molten slag[43].

Foamed glass of an alkali metal phosphate is said to be an efficient sequestering agent. It is made by dehydrating the phosphate melt, mixing it then with alkali carbonates or oxalates, and cooling[44].

Section 9. Many solid foams are available in which the solid phase consists of a high polymer, such as polystyrene (see, e.g., ref. 44a). These foams have very low density and are good insulators of heat and sound. Some commercial products which are used similarly and contain the word foam in their name are sponges rather than foams (see section 5). Because of their low density, synthetic resin foams are valuable in life buoys and life jackets, swimming rafts, fish net floats, and so on. They are good shock absorbers and can serve as packing materials.

Similarly to other solid foams the foams of plastics and elastomers are produced by mixing a gas with a liquid material and then making the liquid bubble walls solid by heat or chemical treatment.

Gas can be incorporated into liquid by mechanical means, for example, by whipping as in the formation of urea-formaldehyde resin foam[45], or by injecting air as in a method of preparing foam rubber from latex[46]. Or the liquid is saturated with a gas under high pressure, pressure then is released, and the excess gas separates as numerous bubbles. Such was the procedure recommended by Denton[47]. A "dough" of, for example, 55 parts of rubber, 3.5 parts of sulfur,

9 parts of "vulcanized oil," 13 parts of antimony pentasulfide, 2 parts of ceresin wax, and 17.5 parts magnesium carbonate was saturated with nitrogen at 113°C and 180 atmospheres, kept at this temperature long enough for the "dough" to be partially vulcanized, and cooled; on releasing the pressure the material expanded to, for example, 6 times its original volume. Then it was heated again in the final mold to, for example, 163°; this caused further expansion of the nitrogen in the bubbles and consequently of the whole piece, and also finally vulcanized the latter. Polystyrene foam[48] can be prepared by heating molten polystyrene with compressed methyl chloride (which is soluble in polystyrene melts) and then lowering the pressure.

As in bread, the gas phase can be the result of a chemical reaction. Th. Hancock is credited with using ammonium carbonate to produce multicellular rubber in 1846–1847[49]. Recently, compounds liberating nitrogen became fashionable. Thus[50] a mixture of polyvinyl chloride (48 parts), tritolyl phosphate (32 parts), azodiisobutyronitrile (10 parts) and phenyl monoisocyanate (25 parts) is heated under pressure to 150°C. At this temperature azodiisobutyronitrile decomposes liberating nitrogen: $NC \cdot C(CH_3)_2N{:}NC(CH_3)_2 \cdot CN \rightarrow N_2 + NC \cdot C(CH_3)_2 \cdot C(CH_3)_2 \cdot CN$. After a suitable heat treatment the foam is placed in an atmosphere saturated with water vapor at 40 to 45°. Water reacts with phenyl isocyanate according to the equation $2C_6H_5N \cdot CO + H_2O = (C_6H_5NH)_2CO + CO_2$; carbon dioxide causes further expansion of the foam, while diphenyl urea stiffens the bubble walls. Carbon dioxide is the gas phase also in a solid foam made without heating and without application of high pressure[51]. A hydrated salt, such as $CaCl_2$, $6H_2O$ or $MnCl_2$, $4H_2O$, and an isocyanate are added to an alkyd resin made of 4 moles glycerol, 2.5 moles adipic acid, and 0.5 mole phthalic anhydride. Water of the salt and the excess of adipic acid react with the isocyanate liberating CO_2. Some other chemical reactions giving rise to the gas phase of multicellular plastics are discussed by Lober[49].

The "blowing agent" may be capable of polymerization[52]. Gradual polymerization of the agent may then leave a vacuum in the bubbles.

Plastic foams exist in a wide range of densities. The usual range seems to lie between 0.02 and 0.3 g/cm^3. Commercial polystyrene foams usually have densities between 0.021 and 0.032 g/cm^3 and contain cells 0.1 cm in diameter[53]. The following information is taken from a pamphlet issued by the Dow Chemical Company and refers to the polystyrene foam of this firm. At the density of 0.026 g/cm^3

(1.6 lb/cu ft) the compressive yield strength is 1 to 1.7 bars (15 to 25 lb/sq in.); tensile strength is 3.5 to 5 bars (50 to 70 lb/sq in.); shear strength 1.7 to 2.4 bars (25 to 35 lb/sq in.); compressive modulus 52 to 100 bars (750 to 1350 lb/sq in.); bending modulus 45 to 80 bars (650 to 1200 lb/sq in.); and thermal conductivity 0.00005 to 0.00007 cal./cm sec. °C. (0.23 to 0.30 Btu/sq ft/hr/°F/in.).

A rubber foam of Sponge Rubber Products Company has density from 0.13 to 0.3 g/cm^3 (8 to 18 lb/cu ft) and thermal conductivity of 0.00006 to 0.00007 cal./cm sec. °C (0.27 to 0.30 Btu/sq ft/hr/°F/in.). A foam of hard rubber has a similar density but is more rigid than polystyrene foams; its compressive strength varies between 2 and 28 bars (30 to 400 lb/sq in.).

Section 10. Fibrin foam is used in medicine. It is made by dissolving fibrinogen in citrate buffer solution at pH 6.05 and beating or aerating the solution into foam which has 2.3 times the volume of the solution. Then thrombin (i.e., the agent which transforms fibrinogen into fibrin) is added, and agitation is continued until clotting occurs[54]. Properties and application of fibrin foam have been described[55, 56].

Separation of Suspended or Dissolved Matter by Foam

Section 11. Flotation is the main method utilizing separation by foam. It is discussed in Chapters 11 and 13. Laboratory work on separation of *solutes* by foam is reviewed in Chapter 10.

The application described by Price[57] may be akin to flotation. Foam was found to suppress dust in a colliery better than plain water if equal volumes of liquid were compared.

Separation of sodium oleate from soldium laurate by foaming was patented by Dubrisay[58]. Purification of raw sugar solutions by foaming was claimed[59]. To prepare proteolytic enzymes in solid form, enzyme solutions were concentrated and whipped into a foam, and the foam was then dried[59a].

Instead of collecting foam fractions (see Chapter 10), foaming can be continued and the liquid allowed to drain out until the solutes have become segregated at different levels in the foam[60]. Then the foam column is divided into sections, and the substances accumulated in the various sections are isolated. In this manner fractionation of polypeptides is possible. In the steady state, saponin is found in the

foam column above gelatin, and gelatin above sodium oleate. The internal surface of the tube in which foam is built up can be roughened, allegedly to increase its wettability by foam[61].

Foams Used for Measurement or Analysis

Section 12. Probably the best known use of foam for chemical analysis is in the determination of total hardness of water. The method is attributed to T. Clark (1847). It was admitted among the standard methods of the American Health Association in 1925[62] but not taken over by more recent manuals. It is based on the observation that solutions of sodium soaps do, while solutions of calcium soaps do not foam. A solution containing calcium ions (i.e., "hard water") is titrated with a sodium soap solution until stable foam can be produced by shaking. The amount of soap used up depends on the amount of calcium salts present in the water.

In the standard method valid in 1925, a solution of 100 g Castile soap in 1 liter 80 per cent alcohol is diluted with aqueous ethanol or methanol until 6.40 cc of it are needed to produce permanent foam after mixing with a solution of 0.004 g calcium carbonate in 50 cc and shaking. "Permanent foam" means that "a lather remains unbroken for 5 min. over the entire surface of the water while the bottle (of 250 cc) lies on its side." Clearly, this criterion is related to those discussed in Chapter 2, section 29.

Total hardness is, numerically, the number of parts of calcium carbonate in million parts of liquid; hence, the above $CaCO_3$ solution has total hardness of 80 ppm. The total hardness of an unknown solution cannot be calculated simply by assuming that $\frac{6.40}{80} = 0.08$ cc of the standardized soap solution are equivalent to 1 ppm of calcium carbonate. Even in the absence of any calcium salt, 0.7 cc of the soap solution are required to make 50 cc of water foaming. Hence, only the excess over 0.7 cc is approximately proportional to total hardness; this proportionality is sufficiently accurate when more than 3 cc of soap solution are needed. In this concentration range 1 cc of this solution corresponds to 14 ppm of calcium carbonate (because $\frac{80}{6.4 - 0.7} = 14$).

Alternatively, the standardized soap solution is titrated with calcium chloride solutions containing in 50 cc as much calcium as 0,

1, 2, 3, and 4 mg calcium carbonate. A calibration curve is plotted and then used to find the total hardness of the unknown sample.

If the water sample contains magnesium salts, "false lather" appears. It persists for less than 5 min. Magnesium consumes more soap than does the equivalent amount of calcium. The simultaneous presence of calcium and magnesium salts in natural waters is the main drawback of the determination of total hardness by foam.

Presence of bile pigments in the urine can be detected by the yellow color of the foam. Sometimes amounts of bile pigments or proteins too small to be detected by the customary methods reveal themselves by a higher foaminess of the urine (unpublished observations).

Section 13. Single soap films are used as indicators of the rate of gas flow. At a spot convenient for observation the gas stream is separated into two currents. The main current continues in a wide pipe, while a small, known part of the total gas volume bubbles through a soap solution and then travels along a narrow glass tube. The visible rate of advance of soap films in this tube is a quantitative measure of the velocity of the total gas flow.

Gooderham[63, 64] applied this technique to gas analysis. The gas to be analysed bubbles through a solution capable of foaming, and the rate of movement of the films produced is observed in a glass tube. Then the gas passes through a reagent absorbing, say, constituent A, and the rate of flow of the remaining gas is determined again by bubbling it through a soap solution and measuring the rate of travel of the soap films formed. Further the gas passes through another reagent which eliminates, say, constituent B, and so on. Thus from the velocity of soap films at subsequent steps of the gas passage the amounts of the constituents can be calculated.

In the usual gas analysis air-tight vessels are required to confine the gas. If a frother is present in the solution, the gas liberated carries its "vessel" (i.e., foam walls) with it. This device was introduced by Matsuura[64a]. For instance, magnesium was determined by precipitating $MgCO_3 \cdot (NH_4)_2CO_3 \cdot 4H_2O$ and then decomposing the precipitate with sulfuric acid in the presence of albumin; the volume of froth (having CO_2 as gas phase) is proportional to the original amount of magnesium. Analogously, the amount of ammonium ion was calculated from the volume of froth, stabilized with saponin, produced when NH_4 was oxidized with an alkaline bromine solution to nitrogen.

Bulging of a soap film is a measure of the pressure difference across it (see Laplace's equation in Chapter 1, section 8). If such a film closes the top of a rotating drum whose side walls contain openings, air escapes through these, and the film curves downward. From its curvature the vacuum created in the drum was computed[64b].

Dewar[65] used soap films as detectors of the quality of sound. Various sounds and other air movements caused characteristic patterns in a vertical soap film.

Foam pressure mentioned in Chapter 5 was recommended for controlling such processes as boiling of milk and saturation of limed sugar juices with carbon dioxide[66, 67]. When this foam pressure exceeds a predetermined value, it operates a device which cuts down the heat supply (in the instance of boiling) or the rate of gas injection (in the instance of saturation).

Section 14. Many industrial preparations foam during the course of their customary application, but their foaming capacity has no or only uncertain relation to their performance. Soap is foremost among these products. It has long been believed that the detergent action of soap solutions is connected with their foaminess. Often, foaminess (or rate of drainage) was considered to be a measure of the efficiency of a detergent. The discovery of powerful detergents having almost no foaming ability brought this belief into disrepute. It is well possible that the foam of a detergent is of importance in some, but irrelevant for other applications. Thus the resistance of foam to mechanical deformation (see Chapter 5) may play a part in the action of shaving soap, while the cleaning efficiency of soap is not due to its foam.

It is not clear what effect, if any, foam has in medicinal foam baths.

References

1. Fisher, G. M., U. S. Patent 1,985,491 (1935); *Chem. Abs.*, **29**, 1184 (1935).
2. Vana, C. A. (to DuPont), U. S. 2,481,457 (1949).
3. Loewenstein, L., French Patent 849,855 (1939); British Patent 544,437; *Chem. Abs.*, **35**, 7638 (1941); **36**, 6708 (1942).
4. Etablissements Vermdrel, French Patent 861,352 (1941); *Chem. Abs.*, **42**, 6052 (1948).
5. Karreth, A., British Patent 379,892 (1931); *Chem. Abs.*, **27**, 3295 (1933).
6. Karreth, A., British Patent 368,423 (1929); *Chem. Abs.*, **27**, 3037 (1933).
7. Mattin, H. E., and Timpson, L. G. M. (to Mearl Corp.), U. S. Patent 2,392,936 (1946); *Chem. Abs.*, **40**, 1954 (1946).
8. Luchinskii, G. P., *J. Phys. Chem.* (*U.S.S.R.*), **13**, 302 (1939).

9. Luchinskii, G. P., and Popova, M. I., *Zavodskaya Lab.*, **8,** 552 (1939).
10. Bransky, D. W., and Diwoky, F. F., *Refiner Natural Gasoline Mfr.*, **19,** 75 (1940); U. S. Patent 2,311,625 (1943) (to Standard Oil Co. of Indiana).
11. Hardenbergh, W. A., "Sewerage and Sewage Treatment," 3rd ed., Scranton, Penna., International Textbook Co., 1950.
12. Micafil, A.-G., Swiss Patent 231,777 (1944); *Chem. Abs.*, **43,** 3186 (1949).
13. Faber, L. D., and Carrell, C. J. (to Faber Engng. Co.), U. S. Patent 1,948,568 (1934).
14. Haefly, H., *Ind. textile*, **55,** 84 (1938).
15. Strauch, C. B., U. S. Patent 2,043,633 (1936).
16. Aero Research, Ltd., DeBruyne, N. A., and Hubbard, D. A., British Patent 549,496 (1942).
17. Marsh, R. D., British Patent 551,488 (1943).
18. Davis, T. L., "The Chemistry of Powder and Explosives," p. 120, New York, John Wiley & Sons, Inc., 1943.
19. Cornwell, E. D., in DeBruyne, N. A., and Houwink, R., "Adhesion and Adhesives," p. 181, New York, Elsevier Publishing Co., 1951.
20. Barmore, M. A., *Colo. Agr. Expt. Sta., Tech. Bull.*, **13** (1935).
21. Lode, A., *Z. Untersuch. Lebensm.*, **58,** 311 (1929); *Chem. Abs.*, **24,** 3064 (1930).
22. Learmonth, E. M., *Food*, **18,** 164 (1949); *Chem. Abs.*, **43,** 5971 (1949).
23. Johnston, N. F. (to R. T. Vanderbilt Co.), U. S. Patent 2,422,486 (1947); *Chem. Abs.*, **41,** 6352 (1947).
24. Lenderink, J., U. S. Patent 2,522,050 (1950).
25. Mars Confection, Ltd., Horlick, Ltd., Beeching, E. I., and Severn, G. W. C., British Patent 560,840 (1944); *Chem. Abs.*, **40,** 3842 (1946).
26. Sair, L., and Rathman, R. (to Central Soya Co.), U. S. Patent 2,502,482 (1950).
27. Turner, J. R. (to Central Soya Co.), U. S. Patent 2,489,208 (1949).
28. Long, B. (to Soc. Saint-Gobain, Chauny & Cirey), U. S. Patent 1,945,052 (1934).
29. Slater, G. (to Owens-Illinois Glass Co.), U. S. Patent 2,119,259 (1938).
30. Long, B. (to Soc. Saint-Gobain, Chauny & Cirey), U. S. Patent 2,123,536 (1938).
31. Sanders, V., *Chem. Eng. Progress*, **44,** 804 (1948).
32. Lytle, W. O. (to Pittsburgh Plate Glass Co.), U. S. Patent 2,237,037 (1941).
33. Fox, J. H., and Lytle, W. O. (to Pittsburgh Plate Glass Co.), U. S. Patent 2,261,022 (1941).
34. Ford, W. D. (to Pittsburgh Corning Corp.), U. S. Patent 2,514,324 (1950).
35. Kreidl, E. L., *Glass Ind.*, **23,** 263, 304, 340 (1942).
35a. Kitaigorodskii, I. I., *Steklo i Keramika*, **1950,** No. 4, p. 3; *Glass Ind.*, **31,** 631 (1950).
36. Rice, J. A. (to Bubblestone Co.), U. S. Patent 1,717,319 (1929).
37. Rice, J. A. (to Bubblestone Co.), U. S. Patent 1,856,294 (1932).
38. King, G. D. (to U. S. Gypsum Co.), U. S. Patent 1,907,982 (1933); *Chem. Abs.*, **27,** 3797 (1933).
39. Winston, J., and Weinstein, F. L. (to Standard Oil Dev. Co.), U. S. Patent 2,507,131 (1950).

40. Ericson, R. (to U. S. Gypsum Co.), U. S. Patent 1,937,472 (1934).
41. Maguire, M. J., U. S. Patent 2,370,058 (1945).
42. Wahlin, B. G. (to Svenska Cellulosa Aktiebolaget), U. S. Patent 2,481,959 (1949); *Chem. Abs.*, **44,** 839 (1950).
43. Gallai-Hatchard, M., U. S. Patent 2,443,103 (1948).
44. Liddell, R. W. (to Hall Laboratories, Inc.), U. S. Patent 2,569,936 (1951); *Chem. Abs.*, **46,** 699 (1952).
44a. Abbott, J. A., *Chem. Eng.*, **59,** No. 7, p. 212 (1952).
45. Meyer, L. S. (to Libbey-Owens-Ford Glass Co.), U. S. Patent 2,384,387 (1945).
46. TeGrotenhuis, T. A., U. S. Patent 2,307,082 (1943).
47. Denton, G. P., U. S. Patent 1,905,269 (1933).
48. Munters, C. G., and Tandberg, J. G., U. S. Patent 2,023,204 (1935).
49. Lober, F., *Angew Chem.*, **64,** 65 (1952).
50. Carpentier, P. J., U. S. Patent 2,576,749 (1951).
51. Simon, E., and Thomas, F. W. (to Lockheed Aircraft Corp.), U. S. Patent 2,577,279 (1951).
52. Sachs, C. C., *Modern Plastics*, **23,** No. 4, 173 (1945).
53. McIntire, O. R., and Kennedy, R. N., *Chem. Eng. Progress*, **44,** 727 (1948).
54. Bering, E. A. (to U. S. A.), U. S. Patent 2,492,458 (1949); *Chem. Abs.*, **44,** 2184 (1950).
55. Bering, E. A., *J. Clin. Invest.*, **23,** 417 (1944); *Chem. Abs.*, **38,** 5937 (1944).
56. Bailey, O. T., and Ingraham, F. D., *J. Clin. Invest.*, **23,** 591 (1944); *Chem. Abs.*, **38,** 5937 (1944).
57. Price, F. H., *Trans. Inst. Mining Engrs. (London)*, **105,** 244 (1946); *Chem. Abs.*, **40,** 6236 (1946).
58. Dubrisay, R., French Patent 747,755; *Chem. Abs.*, **27,** 5124 (1933).
59. Dole, R. A., and McBain, J. W. (to Chemical Process Co.), U. S. Patent 2,162,379 (1939).
59a. Kauffmann, F. L., and Urbain, W. M. (to Swift & Co.), U. S. Patent 2,492,580; *Chem. Abs.*, **44,** 3549 (1950).
60. Kodak-Pathé, French Patent 859,735 (1940); *Chem. Abs.*, **42,** 3225 (1948).
61. Kodak-Pathé, French Patent 942,087 (1949); *Chem. Abs.*, **44,** 10391 (1950).
62. "Standard Methods for the Examination of Water and Sewage," 6th ed., p. 28, New York, Amer. Public Health Assoc., 1925.
63. Gooderham, W. J., *Analyst*, **72,** 520 (1947).
64. Gooderham, W. J., *Anal. Chim. Acta*, **2,** 452 (1948).
64a. Matsuura, N., *J. Chem. Soc. Japan, Pure Chem. Sect.*, **71,** 168, 375, 458 (1950); *Chem. Abs.*, **45,** 4600, 6527 (1951).
64b. Satterly, J., *Am. J. Physics*, **19,** 448 (1951).
65. Dewar, J., *Proc. Roy. Inst. Gt. Brit.*, **24,** 197 (1925).
66. Brukner, F., and Area-Regler, A.-G., German Patent 550,238; *Chem. Abs.*, **26,** 4113 (1932).
67. Schiebl, K., *Z. Zuckerind. čechoslovak. Rep.*, **55,** 476 (1931); *Chem. Abs.*, **26,** 1469 (1932).

15. CHEMICAL ANTIFOAMING AGENTS

C. C. Currie

Dow-Corning Corporation, Midland, Mich.

Section 1. The preparation of this chapter was undertaken with the hope that a survey of the literature might reveal a trend in the effectiveness of defoamers. Just as the polyamides are excellent defoamers for boiler feed water, another class of chemicals might be most effective in controlling foaming of paper pulp and still another type would defoam latex coating compositions most efficiently. In other words, it was hoped that chemical types might show a certain specificity in their action toward foams. If this hope were realized, the whole problem of selecting the correct defoamer for a foaming problem would be simplified.

Because of several complicating factors this rather ambitious hope was not realized. First, the action of a foam inhibitor cannot be predicted by analogy, and generalizations can be misleading. For instance, a very effective defoamer for latex paints is much less effective in the latex alone. Second, the literature is not specific enough to be of much help in finding a logical relationship between effective concentrations and type of foam. For example, a great many defoamers are said to work in processing of sugar beets, but no reliable indications of relative effectiveness were found.

The processing of sugar beets is an excellent example of why a third, and perhaps most important, variable complicates the problem of finding valid relationships between foams and defoamers. In beet-sugar refining the beets will vary in types and concentrations of foam-producing impurities. Each day or sometimes every few hours the processor may find that he must destroy a foam different in chemical and physical properties. When the problem of inhibiting foaming in one mill is multiplied by the number of mills processing beets and using different equipment, raw materials, and techniques of operation, the reader will appreciate the variables which may exist among foams of the same type.

Many factors enter into the choice of the best defoamer for a specific foaming problem. Superficial analysis of a foaming problem may suggest that the best defoamer is the one which is most effective at the lowest concentration. This is not always true. A few of the points which may be important in choosing a foam inhibitor are discussed in the following paragraphs.

In the production of antibiotics a defoamer is worthless if it inhibits the growth of the microörganisms responsible for synthesis of the antibiotic. The defoamer must be stable during sterilization and must maintain a high level of effectiveness during the whole period of aeration. In food processing a defoamer with questionable toxicological properties is an anathema. In the protective coating field a foam inhibitor must not cause "fish-eyes" in the finish and it must act rapidly to break a myriad of tiny bubbles while the coating can still flow.

In many instances odor may be of paramount importance. In the sizing of paper for cigarette packages the defoamer must not impart an odor to the size and subsequently to the cigarettes. Similarly the antifoam should not contaminate or react with the finished product.

Usually the defoamer should be effective for long periods of time, but in packaging of liquid detergents the antifoam should prevent foam only during the filling operation. The detergent, like beer, must foam when the consumer gets it.

Cost, too, must be considered. One defoamer may be twice as effective but three times as expensive per unit of weight as a second antifoaming agent. Conversely an expensive antifoam may be so effective that it costs less to use than larger amounts of a cheaper foam inhibitor.

Section 2. The preceding paragraphs have presented a few of the factors which may have to be considered in employing a defoamer. The remainder of this chapter may provide the reader with a starting point in his search for an antifoaming agent in his foaming problem. Several chemicals may appear to be equally effective in controlling foam; so the reader will have to decide for himself which defoamer most nearly meets his requirements. The data collected in this chapter may eliminate some, but not all, of the work required to select a foam inhibitor.

The chapter is divided into two sections. The first section consists

of a survey of the literature relating to chemical antifoams and is further subdivided into a classification of the defoamers by chemical types. As far as possible the type of application where a given class of defoamers is effective is consolidated. It is probable, however, that suitable defoamers for a specific problem will be found in more than one chemical class. Ross[1] in his excellent report on antifoaming agents also found that more than one chemical type was effective for the same foaming system.

The second part of the chapter lists some of the commercial foam inhibitors. A few instances where these defoamers are used successfully and the concentrations recommended by the manufacturer are given. No attempt is made to rate the relative effectiveness of these defoamers.

Literature Survey

Section 3. Fats, Oils, Waxes, and Other Natural Products. One of the earliest classes of chemicals used for foam inhibition was fats and oils of vegetable or animal origin. Castor oil[1a, 2] was said to be effective in boilers of locomotives using water containing high concentrations of sodium salts together with finely divided solids. There was much debate concerning the relative effectiveness of castor oil. Anderson[3] suggested that many oils other than castor oil were valuable as foam inhibitors, but French[4] insisted that castor oil was the only antifoam for boiler waters. Barber[5] suggested that 5 to 10 ppm of a tannin-castor oil emulsion showed superiority over castor oil alone. Other workers[6] also suggested an emulsified form of castor oil.

In the sugar processing industry castor oil and raw linseed oil[7, 8] were found to be superior to the polymerized or blown oils[9] in defoaming molasses. In the cooking of beet juices to produce sugar, linseed oil, rapeseed oil, and emulsions of either with a mineral oil were tried,[10, 11] but there was much disagreement on the effectiveness of these foam inhibitors. One article[12] suggested that several oils be kept in the plant so that when one failed, another could be tried. Stanek and Vondrak[13] tried wool fat, coconut oil, bone oil, and animal fat in seventeen mills and found the latter three to be the best.

Sulfated olive oil[14] was added to fermenting wort where it proved effective, but in distilling columns or in foam formed during liming or saturation of juices this reagent apparently failed to act as a foam inhibitor. An emulsion containing droplets of oleic acid ranging from

1 to 10 microns in diameter plus solar and mazut oils[15] was used to defoam a molasses mash in production of yeast.

Pine oil together with cyclohexanol and tetrahydronaphthalene has been used to defoam cutting oil emulsions[16]. Sulfated shark liver oil, fish oil, or seal oil, neutralized with an alkali, have been used for the same purpose[17]. Wells[18] found that when an emulsion containing kerosene, mahogany soap, linseed oil, and water was added to paper stock, it kept down the foam on a paper machine. Fife[19] claims that a mixture of vegetable and animal oils acts to suppress foam during the scrubbing of gas by bubbling it through an amine solution.

Mineral oils[20], oil of lavender, pine oil[21], and oxidized high molecular weight hydrocarbons[22] have been disclosed as defoamers for glue and size. In paper making the use of protein (gelatin, casein) and dextrin in formulations often causes severe foaming. Petroleum, milk fat, peanut oil, oil of cloves, vegetable oils, and whale oil[23] were found to decrease the foaming. The use of solvents such as esters, ketones, alcohols, and phenols together with oils and fats[24] is another method of decreasing foam in paper and cardboard manufacture.

In a vapor phase extractive process for recovery of C_4H_6 from C_4H_8 hydrocarbons, mineral oils and fatty oils[25, 26] have been used to prevent foam. In recovery of sulfuric acid, a hydrocarbon extracted from a "coastal distillate" with phenol[27] is effective at concentrations of 5 to 80 ppm. A heavy tar oil[28] is suggested as a foam preventative in naphthalene scrubbers. To control foaming during evaporation of brines containing potassium salts, a combination of petroleum distillate and chlorine gas[29] was used. Mineral oil has been used to inhibit foam in refrigerating brines[30], in antifreeze concentrates[31], and in grinding pigments and insoluble dyes in aqueous media[32].

Sulfated animal, vegetable, and mineral oils[33] have been tried in beet-sugar refining. Milk fat has been used for a number of years as a defoamer; an article by Leviton and Leighton discusses its mode of action[34]. Degras[35] and molten lard[36] are used to control foaming during fermentation reactions. Degras dissolved in naphtha[37] is used to control foaming of apple washers. Degras was used because it is low priced, does not interfere with removal of spray residue, leaves apples in good condition, and is effective in both dilute alkali and acid.

Various waxes and combinations of waxes with other chemicals are suggested as defoamers for soluble cutting oils. Such oils are aqueous emulsions of mineral oils and contain surface-active agents such as alkali naphthenates, sulfonates, and amine soaps. The wax

of an acid containing 22 or more carbon atoms is suggested in concentrations of 0.001 to 5 per cent as a foam inhibitor[38] for this purpose. Vegetable waxes such as candelilla, carnauba, raphia, cottonseed, and palm were found to be effective in concentrations of 0.001 to 5 per cent[39, 40], but Showalter[41] claimed that aluminum stearate is more effective than carnauba or candelilla waxes. A combination of mineral oil, montan wax, and an oil-soluble metallic soap and an ester[42] is claimed to be an effective foam inhibitor. Formulations to suppress foaming during removal of low polymers and monomers from butadiene-styrene latex and chloroprene latex are disclosed by Zimmer[43]. He says that a mixture of 0.08 candelilla wax, 0.24 light petroleum and montan wax in spindle oil is effective in the butadiene-styrene latex. For defoaming the chloroprene latex a mixture of Japan wax, calcium, aluminum, zinc, or magnesium linoleates with zinc oxide or talc is said to be an excellent antifoaming agent.

A patent[44] claims that a mixture of montan wax and lard oil suppresses foaming in glycerol-water antifreezes. Beeswax added in excess of its solubility controls foaming during extractive distillation with furfural solvent[45]. Finally an aqueous emulsion containing glyceryl oleate or stearate and from 0.12 to 1.5 per cent mineral wax is claimed[46] to control foaming of pulp and paper stock.

Phosphatides of vegetable or animal origin are said to be effective in controlling foaming during paper manufacture[47], in sugar refining[48], and in producton of margarine[49].

Section 4. Aliphatic Acids and Esters. In a series of studies of ore flotation, Lubman[50] used ethyl acetate and diethyl malonate to control foaming. The sulfonated ester of a mono- or polycarboxylic acid and an aliphatic alcohol having one or more tertiary carbon atoms is claimed[51] as a foam inhibitor. An example of this type of chemical is sulfonated isobutyl carbinol stearate. Buc[52] claims that a concentration of stearic acid equal to 0.2 to 2.0 per cent of the emulsifier present will control foaming of oil-in-water emulsions. Frothing of drilling muds containing a basic dye such as methyl violet and positively charged mineral particles such as bentonite can be inhibited by addition of 0.05 to 1 per cent diglycol laurate or oleate, isoamyl stearate, or glyceryl monoricinoleate[53]. Fiske[54] suggests isoamyl isovalerate to control foaming of protein, soap, and similar solutions.

Water-base paints such as casein paint foam on application with

the result that pin holes are left in the paint after the paint dries and the bubbles break. One patent[55] discloses that 0.5 to 2 per cent diethyl phthalate will cause destruction of this troublesome foam. An emulsion[56] containing stearic acid, a glycol or polyglycol ester of a fatty acid, or an insoluble metal soap, and an emulsifying agent is claimed to be an effective foam inhibitor for glue solutions, paper pulp suspensions, fermentation masses, and starch pastes during processing and evaporation. Apparently a polyethylene oxide ester is superior to ethylene glycol or propylene glycol esters. Glyceryl monohydroxystearate in combination with a hydrophobic fat or mineral oil or wax is used to inhibit foaming of glue, adhesives, and sizings[57, 58]. A mixture of a fatty acid from soybean, coconut, or peanut oil (30 to 40 per cent) and a naphthenic, asphaltum, or paraffin base hydrocarbon[59] is suggested for use in liming and carbonating beet-sugar juice before filtering to eliminate foam during the filtering step. This mixture may also be used before and during vacuum evaporation. Lauric acid[60] is suggested in beet-sugar distilleries.

Addition of viscosity index improvers such as oil-soluble polyacrylates increases foaminess of lubricating oils. When such oils are used where they are subject to agitation, such as in gears, severe foaming may result. One patent[61] claims that 0.1 to 5 per cent of an oil-soluble, hydroxyl-containing ester of a polyhydric aliphatic alcohol and a long-chain fatty acid will overcome this foam. Examples are glyceryl monostearate and polyglycol palmitate. Another patent[62] suggests addition of 0.05 per cent of an amyl acetate dispersion of the acetyl and the butyl ester of sulfonated ricinoleic acid to gear oil containing extreme pressure agents. Ethyl oleate, butyl stearate, and phenyl stearate are suggested as antifoaming agents for alcohol antifreeze mixtures[63].

Fatty acids and esters have been used in the food industry to eliminate or reduce foam in a variety of processes. For example, a gum guaiac, monostearin solution is used in shortening[64], and a mono fatty acid ester of hexitol polyoxyethylene is used to reduce foam in solubilized oleo resins and essential oils and in processing food products[65]. An ethyl ester of a fatty acid is suggested[66] as a foam inhibitor for coconut oil used in frying. A higher fatty acid is claimed[67] to be an antifoam in jelly making. The foaming of egg whites is suppressed during the drying operation by addition of 0.01 per cent of an ester and 0.022 to 0.004 per cent of a proteolytic enzyme[68]. Two of the esters

cited are glyceryl oleate and erythrol stearate. The enzyme may be papain, trypsin, or bromelin.

In distillation of volatile monomers from aqueous polymer dispersions, acetic acid[69] was found to be a foam suppressant.

Section 5. Alcohols. The alcohols are a versatile group of foam inhibitors. They have been used with success in analytical methods and various industries. For example, one part of hard paraffin, two parts of heavy paraffin oil, and two parts of octyl alcohol were used[70] to inhibit foaming during aeration of oysters, clams, and scallops to determine free nitrogen. A solution of isoamyl alcohol in acetone is used as a defoamer in determining saponins. One to three drops of hexanol were satisfactory in reducing foaming during determination of carbon dioxide in baking powder[71]. Bernhard[72] suggests a mixture of two parts of kerosene with amyl alcohol as an excellent defoamer. Octyl alcohol, one of the best known foam inhibitors, was used in the determination of heat of reaction between oxygen and hemoglobin[73], in paper making[23, 74], in gelatin glues[75], in animal glues[20, 76], in fermentation processes such as production of yeast[77], and in electroplating baths[78]. A mixture of 2-ethylhexanol, 2-propanol, and *p*-tertiary-amylphenol is claimed to be effective at concentrations of 0.01 to 0.5 per cent in viscose solutions, gelatin solutions, textile reagents, dye baths, and printing pastes. Apparently a mixture of glycol and 2-ethylhexanol can be used with little loss in effectiveness[79].

High molecular weight alcohols obtained from synthesis of methanol by pressure reaction of hydrogen and carbon monoxide are said to be effective defoamers for paper coating mixes[80, 81]. Boiling points of these alcohols may range from 133 to above 200°C. A mixture of 6 parts petrolatum, 2 parts sesame oil, 1 part decalin, and 1 part amyl alcohol is claimed to control foaming of paper pulp stuff[82]. A concentration of 500 ppm of the mixture appears to be effective.

Lauryl alcohol[83] or a mixture of cetyl alcohol, glycol tolyl ether, and methyl cyclohexyl adipate[84] is said to be an antifoaming agent for glue solutions and adhesives of animal and vegetable origin. Meyer[85] found that acids were more effective than the corresponding alcohols for defoaming glue solutions. He also suggested for a given homologous series that effectiveness increased with increasing molecular weight.

It is claimed that a liquid mixture of a solid aliphatic alcohol and a liquid aliphatic alcohol will suppress foam in yeast production[86]. A formula consisting of equal parts of hexadecanol, tetradecanol, and paraffin oil is used as an example.

In compounded lubricating oils, Borsoff and Clayton[87] claim methyl salicylate and *o*-hydroxybenzyl alcohol as defoamers. They also say that these chemicals have a more pronounced effect at elevated temperatures.

In aqueous systems such as leather finishes, water-base paints, and alkaline solutions, alcohols seem to be effective foam suppressors. Higher alcohols[88], mixtures of sodium carbonate (50 to 75 per cent) with di(tertiary-amyl)phenoxyethanol or the corresponding 2-propanol or 1-propanol derivatives are reported to be effective[89]. The phenoxy alkanols can be formulated to suppress foaming in commercial bottle-washing machines, soap manufacture, and distillation of aqueous systems. An example[90] is di(tertiary-amyl)phenoxyethanol (30 parts) with a dispersant such as lecithin or a sodium petroleum sulfonate (10 parts) plus a carrier such as aliphatic ketones or alcohols (40 parts) and water (20 parts). A formulation of this type is effective in concentrations as low as 0.001 per cent. A companion patent[91] claims the chemicals alone as inhibitors and in addition to the phenoxy alkanols lists diamylphenol and trioctyl phosphate.

Oleyl alcohol has been discussed as a foam preventative in the Girbotol process[92]. It is reported that removal of hydrogen sulfide and carbon dioxide from natural gas with monoethanolamine solutions is hampered by foaming. Use of oleyl alcohol at concentrations of 10 to 15 ppm increased rate from 14 to 50 million cu ft of gas per day by eliminating foaming[93]. Dodecyl alcohol has been found to reduce foaming of hydrocarbons during treatment with used solutizer process solutions[94].

Octadecanol or dodecanol containing barium hydroxide[95] reduces foaming in a reaction mixture. Dihydric alcohols, too, are used as foam inhibitors. For instance, high molecular weight dihydric aliphatic alcohols with hydroxy groups on adjacent carbon atoms[96], 1,3-glycols or their hydroxy alkyl ethers[97], as well as mixtures containing propylene glycol, triethanolamine, and ethyl acetoacetate[98] have been patented as antifoaming agents. Derivatives of dialkylcyclohexyl glycols such as 1-(3,5-dimethylcyclohexyl)-1,3-butanediol are the subject of one patent[99].

Section 6. Sulfates and Sulfonates. Surface-active agents such as alkali metal salts of sulfated alcohols and salts of sulfonic acids have been used for foam control in the field of petroleum production. In extracting weak acids such as hydrogen sulfide from hydrocarbons containing "sour" gasoline distillate, an alkaline solution of oil-insoluble alkali salt of organic sulfonic acid or sulfate ester acid has proved useful in controlling foam[100]. Both water-soluble[101] sulfonic acids and oil-soluble "mahogany" sulfuric acids[102] are useful in recovery of sulfuric acid. The water-soluble organic acid is generally used in a concentration range of 0.1 to 0.5 per cent by volume. Acidol-soap naphtha obtained by reaction of kerosene alkali waters with sulfur dioxide is useful in drilling muds[103].

In the synthesis of alkyl chlorides from hydrochloric acid and an aliphatic alcohol, the petroleum sulfonates, the salts of alkyl aromatic sulfonic acids, and sodium sulfosuccinic esters are effective at concentrations of 5 to 25 ppm[104]. Sodium lauryl sulfate is useful in deep fat frying using cottonseed oil[105]. Turkey red oil is reported as a foam inhibitor during the fermentation and distillation steps in the production of rum[106].

Section 7. Fatty Acid Soaps. Sodium stearate sprayed on the web forms an insoluble calcium soap and is effective in controlling the foaming of a paper stock containing rosin size and calcium resinate[107]. A mixture of aluminum stearate and a paraffin solvent is useful in paper coatings[108]. For defoaming glue[109] a dispersing agent such as sulfonated tallow is usually employed.

Aluminum, barium, calcium, or zinc oleates or stearates are dissolved in pine oil. These solutions are claimed to be effective foam inhibitors for aqueous glue mixtures used as pigment carriers, shellac, borax solutions for leather dressing, gum solutions, boiler feed water, and calcium chloride solutions used for refrigeration[110]. Aluminum stearate dissolved in stearic acid and diluted with paraffin wax is reported to defoam glue solutions[111, 112]. A water-insoluble soap together with oxygen-containing compounds boiling above 195°C is found to be effective during such operations as leather dressing[113]. Black[105, 114] reports that alkaline earth metal stearates are efficient defoamers in deep fat frying. Alkali resinates and the sulfo resinates are excellent foam inhibitors[115] for lime, cement mortars, and concrete containing colloidal albuminous substances.

Gear oils or roller bearing oils subjected to violent agitation during service foam severely. Aluminum stearate[116] at concentrations of 0.05 to 3 per cent and potassium oleate[117] at 0.5 per cent are used to inhibit this foaming. The latter soap is claimed not to interfere with the lubricating qualities of oils containing sulfurized sperm oil as an extreme pressure additive. Calcium soaps of wool oleins at 0.01 to 0.1 per cent and sodium alkyl esters of sulfuric acid 0.1 to 0.5 per cent are claimed for the same purpose[118].

Sodium stearate is reported as a defoamer in the process of scrubbing exit gases from an oxidation process to produce acetic acid[119]. An alkali metal salt of a rosin acid plus crude oil is claimed to reduce foaming of drilling muds[120]. A dispersion of metallic soaps containing 50 per cent water, a fatty acid, and a polyethylene glycol is reported to be an antifoaming agent[121]. In preparing ketones by heating fatty acids with catalysts, chromium and calcium stearates were used to reduce foam.

Section 8. Nitrogen-containing Compounds. Possibly more effort has been put into the development of foam inhibitors for boiler feed waters than any single problem in the field of foam destruction. Early work was largely empirical and antifoaming agents were naturally occurring products such as castor oil, as was pointed out in the first part of this section.

The work of Bird, Denman, Gunderson, and Jacoby in the field of nitrogen-containing defoamers has been outstanding. These men have been successful in developing specific compounds for boiler feed waters and have contributed much to the understanding of the mechanism of foam control. Much of the literature reported in the paragraphs to follow is the work of these scientists.

The amines are recognized as excellent foam inhibitors, but because of their limited stability in high-pressure steam the polyamides have largely replaced them. The alkyl amines such as undecyloctylamine or diamylmethylamine[122] were claimed to be excellent defoamers for boiler feed water. More effective dispersion of an aromatic polyamine was reported to be obtained by mixing the amine with sodium carbonate, dissolving it in a water-soluble liquid, or by emulsification[123]. The use of cornmeal or tannin extract with dioctylamine or dodecylamine was reported[124]. Heptadecylamine combined with tannin extract and cornmeal to yield a gelatinized product is also

disclosed[125] in a patent. Other amines claimed as defoamers for boiler water were ricinoleyl amine[126], and di- or trialkylated amines such as tricetyl amine and tri(9-octadecenyl)amine and certain quaternaries[127]. These latter surface-active agents were added as emulsions or dispersions or in water-soluble solvents. As work progressed in the field of amines, these defoamers became more complex so that such products as (12-cetyloxy-9-octadecene)cetylamine[128] were not uncommon.

The amides have the well-deserved reputation of excellent foam-inhibiting agents for boiler feed water. One of the early patents[129] claimed a fatty acid amide such as stearamide for this purpose. High molecular weight substances with N-substituted amide groups such as ε-palmitoylamino-N-octadecyl-caproamide were mixed with sodium carbonate and added to boiler water[130, 131]. About 0.01 to 1.0 grain per gallon were used.

Perhaps the greatest effort in this field was concentrated on the polyamides. Diacyl derivatives of a polyamine such as hydrazine or an alkylene diamine were some of the earliest synthetic defoamers disclosed for boiler feed waters[132]. Acylated diamines and polyamines obtained by reacting oleic acid and diethylene triamine or decamethylene diamine and myristic acid are reported in a British patent[133]. Another patent[134] claims the waxy condensation products of a higher fatty acid with an aliphatic polyamine. This product is further condensed with a fatty acid and condensation product of $\frac{2}{3}$ mole of a triglyceride and $\frac{1}{3}$ mole of triethylene tetramine. The final product was found to be effective in concentrations ranging from a trace to 50 ppm. The palmitate of the 12-hydroxy-octadecanoic ester of N-(2-hydroxyethyl)-N-hexadecyl-ethylene diamine[135], the dipalmitoyl amide of ethylene diamine[136], and high molecular weight condensation products of ethylene diamine and the dimer of unsaturated acids such as linseed or soybean oil fatty acids[137] are all claimed as antifoaming agents.

Polyamides such as the high molecular weight mono or diacyl derivative of piperazine[138] are reported to be effective. Jacoby and Bischmann[139, 140] concluded that such polyamides as dioleyl piperazine and N,N′-dioctadecyl-sebacamide owed their effectiveness to the ease with which the compound formed hydrogen bonds. N,N′-di-substituted diamides of dibasic acids could be made more effective by addition of sodium carbonate or water-miscible solvent[141]. Still another amide claimed to be a valuable foam controller in steam

generation is a "substituted amino-N-substituted alkanamide" $RCO \cdot NHNH \cdot CH_2CO \cdot NHNH \cdot OCR$[142]. The aliphatic thioamides such as heptadecyl thioamide[143] and disulfonamides of long-chain aliphatic sulfonic acids[144] are also reported to be useful defoamers in boilers.

Other nitrogen-containing chemicals are used to control foaming in a variety of systems. Alkyl pyridinium and alkyl quinolinium compounds[145] or their reaction products with phenols or aromatic nuclear sulfonic acids[146] are suggested as foam inhibitors. Water-insoluble amines such as triamylamine are reported[147] to be excellent defoamers for dye baths. Oxazolines are said[148] to be effective during fermentation and subsurface aeration. Foaming of glue, starch, and casein solutions for paper coating is inhibited by introduction of approximately 1 per cent of the reaction product of a fatty acids with an alkylamine[149]. An example is the cationic surface-active agent obtained by reaction of oleic acid and ethylene diamine. Quaternaries are said to control foaming in synthesis of alkyl amines from the corresponding alcohol[104]. Basic acylated polyamine alcohols are claimed to be good defoamers for an alkali bleaching agent at 4 ppm[150].

The same type of product is effective in a diesel fuel oil at 1 part in 4,000. These polyamine alcohols should be dispersed in water or diluted with aromatic solvent before additon. In lubricating oils, salts of polymeric N-dialkyl-arylamines[151] and nitro and amino alkanols[152] are used. The reaction product of an amine and a sulfonated fatty oil such as aniline with sulfated castor oil is reported to be effective in lubricating oil mixtures in concentrations of 0.01 to 5 per cent[153].

Section 9. Phosphates. Many of the patents concerning the phosphates indicate that they are foam depressants for lubricating oils. Aromatic amine salts of 3-methylbutyl-2-ethylhexyl orthophosphate[154] (presumably identical with "isoamyl octyl phosphate" listed below); primary aliphatic amine salts of dialiphatic substituted monothio phosphoric acids[155]; aniline, dimethyl aniline, or diethyl aniline salts of isoamyl octyl phosphate[156]; quinoline isoamyl octyl phosphate[157]; pyridine isoamyl octyl phosphate[158]; dimethyl pyridine isoamyl octyl phosphate[159]; and nicotine isoamyl octyl phosphate[160] are all reported to reduce foaming of lubricating oils. Concentrations of 0.01 to 1 per cent of a salt of alkyl alkylene diphosphate such as

potassium trioctyl ethylene diphosphate effectively control foam in lubricating oil[161].

Because of the churning action of gears and because of additives, gear oils present a difficult foaming problem. Trioctyl monothio phosphate and tri(2-ethylhexyl)monothiophosphate are said to control foaming of such oils[162].

Neutral phosphoric acid esters are added to a "polyether monocarboxylic acid," such as $C_4H_9OCH_2CH_2OCH_2CO_2H$. This mixture is useful in defoaming mercerizing liquor[163]. Phosphoric acid esters diluted with an organic solvent[164] are useful defoamers. Various phosphates are described by Ross and McBain[165] and found effective in synthetic foaming systems. Water-insoluble phosphate esters are claimed to be more effective when diluted with a water-miscible solvent such as ethanol and acetone[166]. Similarly, tributyl phosphate dissolved in isopropyl alcohol was found to be effective in reducing foaming of soap solutions used for treating fabrics[167].

Section 10. Organo-Silicon and Organo-Germanium Compounds. The silicones are relative newcomers to the field of foam inhibitors, but they have more than made up for lost time. Certain of the silicones approach the goal of a universal antifoam and are used in a variety of applications.

Much of the early work on silicon-containing compounds indicated that the silicones were excellent defoamers for lubricating oils. Early patents[168, 169, 170] list a dihydrocarbon silicone such as dimethylpolysiloxane and polymerized silicates such as diethylsilicate as effective foam inhibitors for lubricating oils. One patent[169] showed that a dimethylpolysiloxane was effective in SAE 50 motor oil at 10 ppm. For storage stability a dispersion of 2 microns or less of the silicone was suggested. Still another patent[171] lists aliphatic silicon compounds containing two alkyl or two alkoxy groups linked directly to the silicone atom. Trautman[172] reports that viscous methyl silicones are effective at concentrations as low as 5 ppm.

Organo-silicon polymers have been found effective in reducing foaming during production of a reversible high-temperature grease[173]. Cyclic organo-silicon condensation polymers are reported[174] very effective in vacuum distillation of lubricating oil stocks, in dehydration of oils, and in soap formation by neutralization of fatty acids. An organo-silicon polymer in which the organic radicals are saturated

alkyl groups containing 14 to 24 carbon atoms, e. g., dicetyl silicone[175], is effective in oil-in-water emulsions at concentrations of 0.05 to 5 per cent. An organo-silicon polymer containing silica is effective in cooking varnish even at 0.05 per cent concentration[176] and in the fermentation step in producing streptomycin[177]. According to a recent patent[177a] this antifoaming agent is comprised of a mixture of silica aerogel and a viscous methyl siloxane polymer.

A silicone oil terminated with hydroxyl groups such as diethyl diphenyl disiloxane diol at concentrations ranging from 1 to 10,000 ppm effectively controlled foam during removal of water from spumiferous materials[178]. For instance, in heating a mixture of petrolatum, hydrogenated fish oils and calcium hydroxide, the addition of 0.001 part of the diol decreased the heating time from 3 to 0.5 hours and the kettle operated at $\frac{5}{6}$ instead of $\frac{1}{3}$ capacity.

Polymeric dimethyl silicones are effective during distillation of volatiles from synthetic elastomeric latices[179]. In concentration of surface-active agents by boiling off water, addition of butyl trichlorosilane or the corresponding ethoxy compound is said to be an excellent defoamer[180] above 80°C. It is believed that upon addition, the reactive silane hydrolyzes to form butyl silane triol. The tri- or tetra-alkyl silanes are dissolved in a combination of a water-soluble and a water-insoluble solvent[181]. A formulation might be tributyl silane, 2-ethyl hexanol, and 2-propanol. This solution is a foam inhibitor for gelatin and viscose solutions used in paper and textile operations or in fermentation. High molecular weight methyl (chloromethyl) siloxanes converted to polyhydric alcohols are claimed[182] as foam suppressants.

Organo-silicon-phosphorus compounds have been reported to be defoamers for oil. Such a chemical containing at least one Si-O-P group with organic groups on Si, P, or both is described in a patent[183]. For example, dichlorodimethyl silane is reacted with sodium ethyl isoamyl phosphate. The reaction product of an organic silicon halide with phosphoric acid or its derivatives is said to defoam petroleum oils[184]. In this latter patent a typical reaction cited is that between disodium ethyl phosphate and dichlorodimethyl silane.

Cyclic trimers of dialkyl germanium oxide are cited[185] as being antifoaming agents for gear, aviation, and diesel oils. Such compounds as dimethyl germanium oxide trimer and diethyl germanium oxide trimer are said to be effective in SAE 50 motor oil at 0.1 to 0.01 per cent. In tests a dispersion in petroleum oil with droplets of 2 to 0.3 microns was used.

Section 11. Sulfides and Thio Compounds. Metallic derivatives of thio ethers and disulfides derived from the orthohydroxy derivative of stearophenone, laurophenone, etc., are mixed with organic phosphite esters to yield a foam-inhibiting agent for lubricating oil[186].

Other sulfur-containing compounds claimed to be effective foam inhibitors are long-chain alkyl thienyl ketones[187], organic compounds containing either sulfur or oxygen for Solutizer process solutions[188]. and mixed thienyl alkyl ketones[189] such as 2-stearoyl-thiophene and 2-lauroyl-thiophene for boiler waters.

Section 12. Halogenated Compounds. Carbon tetrachloride and other liquid aliphatic chlorinated hydrocarbons are said to be effective as defoamers for vegetable protein glues[190,190a]. A halogenated aromatic or aliphatic amine such as the chlorination product of undecylamine which is subsequently hydrolyzed to obtain an hydroxy compound is cited as a defoamer for boiler water[191]. About 35 per cent of this material is mixed with 55 per cent tannin extract, 5 per cent bentonite, and 5 per cent corn starch to aid in dispersion. A polymer of a chlorofluoroolefin is reported to be effective in dehydration of an aqueous mixture[192].

Mineral oils, fatty acids, alcohols, and similar materials which foam during aeration or distillation are reported to be effectively defoamed by addition of a polymeric derivative of chlorofluoro organic compounds with most or all of the hydrogen replaced[193]. An example is trichlorotrifluoropropene polymerized to 10 to 50 carbon atoms.

A fluoro-organic compound was found to possess defoaming characteristics at 0.001 to 10 per cent in compounding the metal sulfonate of a petroleum sulfonic acid in oil[194]. A similar highly fluorinated aliphatic hydrocarbon is reported effective in lubricant compositions containing metallo-organic derivatives and used as pressure transfer media[195]. Concentrations of 0.0001 to 10 per cent of highly fluorinated aliphatic and cyclo-aliphatic hydrocarbons containing 5 to 50 carbon atoms and one more fluorine than carbon atom are said to control foaming in lubricating oil compositions, heavy duty engine oils, in grease making, and in production of metal phenates and phenol sulfides[196]. Completely fluorinated hydrocarbons containing a maximum of 3 per cent hydrogen and 5 to 10 carbon atoms are reported as

effective defoamers for oils containing fumarates, polyfumarate, and polyhydric alcohols[197].

Section 13. Inorganic Compounds. Disodium phosphate is claimed to be a defoamer for a liquid coffee concentrate when it is diluted with carbonated water[198]. The use of peptizing agents such as 10 to 12 per cent of trisodium phosphate with boiler water antifoams is said to aid in promoting an extremely fine state of subdivision and to increase the life of the antifoam so that it is suitable for use in wayside watering tanks for locomotives[199]. A mixture of boric acid, monosodium phosphate, and ethyl carbonate is cited as a defoamer in distillation of styrene from copolymer latex[200].

Alkali salts of sulfuric and sulfurous acids are claimed to be foam inhibitors[201]. It is reported that about 0.5 per cent of magnesium sulfate acts to control foam during Arndt's distillation of nitrates[202]. Ferric sulfate is claimed as an antifoam in cutting oil emulsions[203]. Ferrous sulfate and other soluble iron salts act as defoamers by precipitating soluble frothing agents[204].

Colloidal micelles containing silica and a heavy metal oxide in the ratio of 4 to 1 are claimed to reduce foam formation in boilers[205]. A mixture of 85 per cent (minimum) alkali metal hydroxide, 2 to 6 per cent alkali sulfate, and 3 to 11 per cent soluble alkali silicate is apparently effective in defoaming beverages, metal salts, proteins, and carbohydrates[206]. Holmes[207] suggested sodium aluminate to control foaming of boiler water, Carrick[208] suggests that treatment with sodium carbonate plus frequent boiling will reduce foaming in locomotive boilers.

Sodium carbonate and a coagulant such as an aluminum or iron salt apparently cause precipitation of foam-forming substances in the recovery of acetic acid after acetylation of cellulose[209]. Calcium acetate added to ethylene glycol cooling systems in concentrations of 0.1 per cent or less is claimed to be an effective foam inhibitor[210].

Solid foam inhibitors are also found in the literature. Bentonite, 0.01 to 1 per cent, is claimed to reduce foaming of return water from extraction of sugar-bearing materials[211]. Bauxite is mentioned in coking pitch[212]. Finely powdered carbon is said to be effective in producing phenol salts[213] and Mack[214] reports that a mixture of dry pumice and redistilled oleic acid is helpful during distillation of water from oils.

Section 14. Miscellaneous. An insoluble gas such as air, nitrogen, or natural gas was reported to prevent foaming in steam boilers when the gas was bubbled through the steam-water interface[215]. Frothing of sugar molasses is reduced by covering their surface with water[215a]. Cohen[216, 217] said that application of chlorine to crude influent reduces the foam in Imhoff tanks. Luisada[218] says that ethyl alcohol vapor assists in the therapy of paroxysmal pulmonary edema (foaming in the lungs).

Starch is said to control foaming of paper stock containing an acid-soluble filler[219]. Starch or a starch carbohydrate is claimed effective in boiler water[220]. A tannin extract apparently acts as a synergist with amines in controlling foam in the same use[221]. A mixture of starch, trisodium phosphate, and sodium carbonate is claimed for the same purpose[222].

The foaming of kaolin-casein suspensions used in paper coating is reduced by addition of 2 per cent based on the casein of a rubberine gel[223]. A proteolytic enzyme such as pepsin, papain, or bromelin is claimed to act as a defoamer during the thinning of fermented egg whites[224]. A 0.5 per cent solution of cholesterol in ethanol[225] is helpful in reducing foaming during a micro-Kjeldahl distillation. Raw milk reduces foaming of warm glue solutions[226]. French[227] suggested that tannin combined with other defoamers possessed synergistic action and improved the foam-inhibiting action.

Commerical Defoamers

Section 15. The author was forced to depend to a large extent upon the generosity of the various manufacturers in submitting technical end use information about their defoamers. While every effort was made to include all commercial defoamers, some may have been overlooked; such omissions are due to the author's ignorance and are entirely unintentional.

Wherever possible, these defoamers are grouped according to chemical type.

Section 16. Esters. Chemically, "Diglycol Laurate S"* is diethylene glycol laurate-a straw-colored liquid. It is insoluble, but dispersible in water and soluble in most organic solvents[228]. This ester is

* Glyco Products Co., Inc.

almost odorless which is one reason it has taken the place of pine oil and kerosene in many paper mills.

"Diglycol Laurate S" has been found to be a defoaming agent in coating operations in paper mills. It is especially useful in combating foaming of proteins and as small an amount as 0.1 to 1 per cent based on protein present effectively retards foam. In some paper mills, 20 ppm based on total solids or 8 ppm based on the weight of the entire coating composition including the water, is used. The necessary amount of "Diglycol Laurate S" will vary widely, however. It is reported that this ester is 5 to 6 times more effective than octyl alcohol[228]. It is effective in concentrations seldom exceeding 0.1 per cent.

"Diglycol Laurate S" is also used in foaming problems involving casein, whey, and emulsions[229]. About 10 to 30 per cent "Foamex"* sometimes enhances its defoaming properties.

Other fatty acid esters[228] used to inhibit foaming are "Glyceryl Monoricinoleate S," "Glyceryl Mono Laurate S-547," and "Propylene Glycol Mono Laurate S-1003."* The latter two are used as defoamers in the food industry. Recent indications are that "Glyceryl Monoricinoleate S" may be a defoamer in latex emulsions as well as an auxiliary stabilizer or emulsifier[229].

The preceding chemicals are used primarily in aqueous systems. They do not appear to be satisfactory foam inhibitors for hydrocarbon or other organic solutions. "Polyethylene Glycol 400 Mono Laurate"* shows some promise as a foam inhibitor in specialized problems where foaming is encountered in hydrocarbon solutions. It is interesting to note that this ester is soluble in water, but is poorly soluble in certain hydrocarbons such as mineral oil.

Another ester of importance as a defoamer is "Span 85"† which is sorbitan trioleate. It is a thin oily liquid, amber in color, and is dispersible, but not soluble, in water. It is soluble in most organic solvents[230]. Only small amounts are usually required. For instance, one pint eliminates the foam produced during the manufacture of 1,000 gallons of yeast. Approximately 90 ppm eliminates foam produced in the cooking of the glue gelatin. This product may be used effectively as an antifoaming agent in the preparation of casein coatings for paper application. Here too only a small amount is needed. Too high a concentration will cause "fish eye" formations in the paper. "Span 85" is also successfully employed as a defoamer in the flexible

* Glyco Products Co., Inc.

† Atlas Powder Co.

and plastic glues used for book binding and many other purposes. The actual amount needed depends upon the process. Best results are obtained if the antifoaming agent is used immediately prior to the stage where the foam is usually produced.

"Span 20"* is sorbitan monolaurate[229]. This compound is an oily liquid possessing a red amber color. It is dispersible in water and soluble in many organic solvents. "Tween 20"* is a polyoxyethylene sorbitan monoalurate[230] which is a lemon-orange, oily liquid soluble in water and in many organic solvents. It is used occasionally with oil solutions, but as a general rule this material actually promotes foam in aqueous solutions.

Both of these products have been successfully employed as antifoaming agents in licorice solutions, in protein digests, in evaporation of aqueous solutions and dispersions of organic materials, in operations involving caustic solutions of certain inorganic salts, in yeast manufacturing, in cooking of gelatin, and in phosphoric acid manufacture[231].

In the paper industry the action of beaters and similar equipment enhances foaming. In addition, additives in the furnish may aggravate this tendency to foam. Foaming may be severe enough to be seen or it may consist of a dispersion of tiny bubbles of air in the water. The latter condition may cause trouble in sheet formation. The pH may vary widely in different operations. A foam inhibitor in the paper industry must, first of all, effectively defoam and reduce bubble formation under these conditions. Second, it must be easily added and have no effect on other chemicals in the furnish. Third, it must be nonadsorptive to solids and prefer to stay at the air-water interface where it is needed. Fourth, small concentrations must do a satisfactory job.

According to the manufacturer, "Nalco 71"† meets these four requirements[232]. This foam inhibitor consists of a pale straw colored liquid mixture of glycol and a fatty acid base surface-active agent. In addition, emulsifiers and stabilizers are incorporated to assist in dispersion of the antifoam[233]. This product is mixed with warm water at concentrations of at least 5 per cent and added continuously just ahead of the point where foaming is a problem. Concentrations of 1 to 4 ppm based on the slurry are usually effective in paper mills; other applications may need from 1 to 100 ppm[232]. In the paper

* Atlas Powder Co.

† National Aluminate Corp.

industry, "Nalco 71" is used at the rate of 0.25 to 1.0 lb/ton of furnish and is effective from pH 4 to pH 9.5.

"Nalco 71-D5"* is a liquid mixture consisting of a polyglycol and a fatty acid base surface-active agent, as well as chemicals to promote emulsification and to increase emulsion stability. This product is pale straw in color and possesses a faint aromatic odor[234]. According to the manufacturer "Nalco 71-D5" is recommended to inhibit foaming in extraction of protein and in coating formulations, adhesives, and paper-making processes. In addition, it is said to control foaming in acid cleaning, waste disposal plants, and evaporators. It is not recommended for boiler water[234]. Concentrations may vary from 1 to 200 ppm depending upon the particular foaming system. It should be dispersed and used in the same manner as "Nalco 71."

"Defoamer ED,"† a comparatively new antifoam, is essentially a mixture of high molecular weight esters probably based on coconut oil fatty acids and containing solid particles[235]. When latex paints are applied to a surface with a roller, the formation of foam frequently results in a cratered or blistered surface. This ester is an excellent defoamer for latex paints and thus ensures a smooth coating. It can be dispersed directly into the paint or one of the constituents. Concentrations as low as 0.1 per cent by volume have proved effective. According to the manufacturer, "Defoamer ED" has had some acceptance in the textile field and experimental work is under way in other types of foaming problems[236].

"Nopco KF"‡ is believed to be a mixture of partially esterified glycerin and a wax. It is used as an antifoaming agent in paper making and is added to the slurry as an emulsion. About 0.1 per cent calculated on the weight of the dry pulp is said to be effective.

A chemically similar defoamer, "Nopco 1907,"‡ is used to defoam glues of animal origin when high-speed mechanical application of the glue may cause excessive foaming.

Section 17. Polyamides. The polyalkylene polyamides are recognized as excellent foam inhibitors in aqueous systems, particularly in high-pressure steam boilers. Not only do these chemicals inhibit foam, but they also aid in steam purification by reducing entrainment

* National Aluminate Corp.
† El Dorado Oil Works.
‡ Nopco Chemical Co.

of water in the steam in the form of an aerosol. Usually 0.2 to 2 ppm are sufficient to do an excellent job. One of the preferred polyamides for commercial use is tetranaphthenoyl triethylene tetramine[237]. This chemical is an amber, high-boiling, very viscous liquid insoluble in water, but soluble in most organic solvents.

In practice the polyamide is seldom used alone. Usually it is added as an emulsion in combination with various synergistic agents such as tannins. In addition, alkali salts are usually mixed into the formulation to aid in dispersing the compound in boiler feed water[238, 239].

These polyamide formulations are said to reduce entrainment of water in steam; to possess excellent foam-inhibiting properties; and to be long lasting and effective in any type of water. In addition, they are reported to promote formation of individual steam bubbles on the heater surface and thus provide maximum heat transfer and wetting at the metal-water interface. They can be introduced with regular water treatment[240].

Dearborn treatment* No. 659 is a powder and No. 693 a briquette. The former is introduced as a dilute dispersion in water while No. 693 can be added directly by means of a feeder bypass line. Other polyamide defoamers are No. 666, a powdered medium organic alkaline treatment; No. 690, which is No. 666 in briquette form; and No. 640, a caustic paste medium organic alkaline treatment. These formulations are intended to inhibit foaming of high-pressure boilers. For low-pressure boilers and evaporators No. 662, a powdered combination antifoam and antiscale agent, is suggested[240].

"Nalco 70"† is a dark amber liquid of the acylated polyamide type[241]. It possesses an odor of tannin. This antifoam is not dilutable with water, but can be diluted with a solvent for feeding to the foaming system.

This chemical is used to inhibit foaming at high pH and from 1 to 50 ppm are usually required. It is reported by the manufacturer to be effective in paper mill digesters employing either the sulfite or sulfate process; also in sewage effluents and in processing caustic[240].

Section 18. Alcohols. "Foamacide L"‡ is an antifoam agent based on ditertiary amyl phenoxyethanol[242]. Not much information

* Dearborn Chemical Co.

† National Aluminate Corp.

‡ Wyandotte Chemical Corp.

is available in the literature concerning the uses of this agent, but it has been employed successfully to control foaming in bottle washers.

The "Ucon" oils* may be considered as monohydric alcohols. These polyoxyalkylene fluids range in molecular weight from 300 to 15,000 and are a family of polymers rather than a single product. They are said to possess foam-inhibiting properties for aqueous solutions, petroleum oils, and organic liquids[243]. Apparently they are most effective in hot aqueous solutions and in suspensions of solids in liquids. Their effectiveness in hot aqueous systems may be related to their reverse solubility characteristics. That is, the HB series in particular becomes less soluble in water as the temperature is increased. The HB series was recently reported to be effective in controlling foaming of boiler feed water. The reverse solubility property just mentioned may cause this type of antifoaming agent to act at the water-steam interface.

The manufacturer further suggests[243] that a mixture of "Ucon 50-HB-3520" and heptanol-3 is a more effective antifoaming agent for a liquid soap formulation than is either chemical alone.

"Monsanto AE-1"† is a high molecular weight alcohol containing an ester linkage. It is a light-brown viscous liquid with a flash point of about 315°F. and a boiling point of 225°C at 15 mm of mercury. It is insoluble in water, but soluble in most solvents[244].

"Monsanto AE-1" has been reported[245] to be effective in controlling foam in production of ethyl alcohol from molasses where about one quart (4 ppm) is charged to a 60,000-gal fermenter. During distillation of beer, about 33 ppm of "AE-1" is added dropwise at the suction pump feeding the still. One quart (270 ppm) is effective when added to 7,000 to 8,000 lb of wet glycerin, the batch being heated to 180°F. at 28 in. of vacuum in order to evaporate the water. About 1.5 oz of this product in 300 gal of 3 per cent caustic soda solution, used in a Miller-Hydro bottle washer, controls foaming effectively. In yeast production and various other fermentations, "AE-1" is said to be an effective defoamer at 50 to 500 ppm. About 0.5 to 1.5 per cent is incorporated in polystyrene latex, water dispersions, paints, and coatings to control foaming. In general, it is said to be an effective defoamer at 50 to 500 ppm.

Other commercially available alcohols which possess foam-inhibiting properties are 2-ethylhexanol, undecanol, tetradecanol, and heptadecanol. The first mentioned alcohol has been used to control foaming

* Carbide and Carbon Chemicals Corp.

† Monsanto Chemical Co.

in the varnish, photographic, ceramic, and paper-coating industries[246]. The latter three agents are used when high-boiling antifoaming agents are necessary. In production of penicillin, heptadecanol has been used to control foaming during fermentation[246].

Section 19. Silicones. The silicones represent an entirely new class of chemical compounds which, in spite of their newness, have achieved rapid acceptance as exceptionally effective foam inhibitors.

The commercial forms of the silicones are water-insoluble methylpolysiloxane fluids, a silicone fluid containing silica, or an emulsion of either. The methylsiloxane containing finely divided silica is generally described as a compound to differentiate it from the silicone fluids and is more generally useful than the silicone fluids.

The fluids are useful primarily in nonaqueous systems. A few of the uses and the concentration ranges found effective are in lubricating oils, 1 to 10 ppm; asphalt and tar, 4 to 10 ppm; varnish cooking 1 to 40 ppm; and in vegetable and animal fats and oils, 1 to 40 ppm.

The compound is useful in either aqueous or nonaqueous systems. Concentrations necessary for foam control may vary from 0.25 to 100 ppm. For instance, processing of tars and asphalts may require 0.25 to 5 ppm; fats, 4 to 10 ppm; resins and varnishes, 0.5 to 40 ppm; and detergents and similar surfactants, 40 to 100 ppm. Usually the compound is dispersed in a solvent before adding to the foaming system.

"Antifoam A"* is a colorless, translucent compound[247] which is practically inert physiologically[248, 249]. Because of this very low order of toxicity it is used to defoam blood during aeration in the artificial lung[250] and is being investigated to control foaming in treating severe cases of pulmonary edema. It is also being investigated as a defoamer in penicillin production[251]. Though insoluble in water, it is dispersible in hydrocarbon solvents. Emulsions of this defoamer for easy dispersion in water are commercially available under the names "Antifoam A Emulsion" and "Dow Corning Antifoam AF Emulsion." The latter contains emulsifiers commonly used in the food processing industry.

The General Electric Company manufactures a somewhat similar compound[252] known as "SS-66." This is a pale gray semifluid product dispersible in many solvents, but insoluble in water[253]. No informa-

* Dow Corning Corp.

tion is available concerning the toxicological properties of this defoamer.

General Electric also produces a series of fluids based on methylpolysiloxane[252]. The most popular viscosity grades of these water-white fluid series are "SF 96 (100)" for viscous hydrocarbons and "SF 96 (500)" for very fluid oils.

Dow Corning manufactures a "200" series of methylpolysiloxanes and suggests the 100 cs. and 1,000 cs. fluids as effective foam inhibitors.

"Foamacide S"* consists of two liquid antifoaming agents adsorbed on a mild alkali carrier[254]. One of the active materials is a silicone[242]. The product has the appearance of a moist powder. It is suggested for use in pressure or hydro-bottle washing machines to reduce excessive foaming. The general recommendation is to add 1 oz of "Foamacide S" to 100 gal of alkali solution with further additions as necessary to inhibit foaming. The defoamer will apparently control foaming satisfactorily without retarding the action of alkali. It is said to be safe to use and easy to handle.

Section 20. Miscellaneous. "Defoamer 4"† is produced in 2½-lb bricks which are dispersed in hot water containing soda ash[255]. The dispersion prior to use contains 0.75 per cent defoamer. Its chemical formulation is not known.

The manufacturer reports that in the diluted state the defoamer has excellent stability providing the brick is dispersed in soft or softened water. Very little information is available on the applications of this foam inhibitor although it has been reported that "Defoamer 4" works effectively as an antifoam during concentration of synthetic latices by distillation.

"Foamex"‡ is a pale yellow liquid which is insoluble in water, but soluble in most solvents[256]. It is suggested for foam inhibition in manufacture of aqueous solutions of glue, casein, gelatin, and shellac. It can be incorporated in the water before making the solution or added to the solution directly. Usually about 1 oz in 10 gal is adequate. In some instances the manufacturer suggests dissolving "Foamex"

* Wyandotte Chemicals Corp.

† Hercules Powder Co.

‡ Glyco Products Co., Inc.

in 2 to 3 parts of "Diglycol Laurate S" before adding to the solution to be defoamed. This technique reduces the tendency to form oil spots.

When photographic film is run through developer solution at high speeds, foam is generated. About 1 oz of "Foamex" to 100 gal of developing solution is sufficient to inhibit foaming.

"Foamex" is being used in many industries to combat foaming in cosmetics, paints, and paper. It is also used to inhibit foaming during the production of various types of emulsions.

Tributyl phosphate[257]* is a colorless liquid very slightly soluble in water, but miscible with many organic solvents. This chemical is used as a defoamer in synthetic latex paints where 1 per cent or less is sufficient to reduce foaming during production, packaging, and application of the paint. Tributyl phosphate is used in the paper industry in concentrations in the neighborhood of 0.1 per cent based on the solids. It leaves no residual odor. This phosphate is useful at low concentrations (100 to 1000 ppm) in controlling foaming of water adhesives and textile sizes, inks, detergent solutions, and casein solutions. It is suggested that tributyl phosphate be dissolved in an alcohol or other solvent and sprayed on the surface of the foam in order to obtain good dispersion and optimum results.

"Nopco 1333," "Nopco 1497," and "Nopco 1497B"† are a series of defoamers reported to contain aluminum stearate as one of the constituents. These agents are apparently most effective in inhibiting foaming of animal glue and textile sizings.

"Defoamer 514" and "Defoamer FTS"‡ are the names given[258] to a sulfonated tallow wax and a liquid fatty acid with mineral oil. The former product is used to inhibit foaming of hide and bone glues. "Defoamer FTS" is a useful antifoaming agent during yeast fermentations. It is also used to some extent in the paper industry.

References

1. Ross, S., "The Inhibition of Foaming," Rensselaer Polytechnic Institute Bulletin, Engineering and Science Series, No. 63.
1a. Foulk, C. W., *Ind. Eng. Chem.*, **16**, 1121 (1924).
2. Matthews, F. J., *Eng. and Boiler House Rev.*, **52**, 388 (1938).
3. Anderson, O. F., *Ind. Eng. Chem.*, **16**, 206 (1924).
4. French, D. K., *Ind. Eng. Chem.*, **16**, 206 (1924).

* Commercial Solvents Corp.
† Nopco Chemical Co.
‡ E. F. Drew and Co., Inc.

5. Barber, E. G., *Eng. and Boiler House Rev.*, **55,** 156, 166 (1941).
6. Gleim, V. G., and Liffaievitch, L. I., *Chimie & industrie*, **39,** 1097 (1937).
7. Vorob'ev, N., *Maslobolno-Zhirovoe Delo*, **9,** 25 (1934).
8. Vorob'ev, N., *Chimie & Industrie*, **32,** 1405 (1934).
9. Mirčev, A., *Listy Cukrovar.*, **56,** 377 (1939).
10. Scheye, H., *Z. Deut. Zuckerind*, **46,** 626, 645 (1921).
11. Haacke, *Z. Deut. Zuckerind.*, **46,** 661 (1921).
12. Mirčev, A., *Listy Cukrovar.*, **53,** 371 (1935).
13. Stanek, V. L., and Vondrak, J., *Listy Cukrovar.*, **48,** 374 (1930).
14. Barti, P., *Bull. assoc. chim.*, **52,** 286 (1935).
15. Metyushev, B. D., and Kharin, S. C., *Gosudarst. Nauch. Issledovatel'. Inst. Kolloid. Khim., Tckhnol. Protsessy i Kontrol Pishchevoi Ind.*, 149 (1938).
16. Shipp, J. H., Bacon, C. C., and Pedersen, C. J. (to E. I. duPont deNemours & Co.), U. S. Patent 2,420,329.
17. Norring, O. (to Shell Development Co.), U. S. Patent 2,285,940.
18. Wells, S. D. (to Institute of Paper Chemistry), Canadian Patent 432,672.
19. Fife, H. R. (to Carbide and Carbon Chemicals Corp.), Canadian Patent 349,127.
20. Schmidt, A., *Farben Ztg.*, **39,** 1131, 1179, 1227 (1934).
21. Meyer, J. B., *Kunstdünger u. Leim*, **28,** 296 (1931).
22. Buch, A., Brunner, K., and Lalleike, H. (to Chemische Fabrik Stockhausen Komm.-Ges.), German Patent 694,242.
23. Belani, E., *Papier-Ztg.*, **56,** 52, 1296 (1931); *Zellstoff u. Papier*, **11,** 554 (1931).
24. Schacht, F., French Patent 793,173.
25. Evans, T. W., and Morris, R. C. (to Shell Development Co.), U. S. Patent 2,373,951.
26. Garrett, B. S. (to Standard Oil Development Co.), U. S. Patent 2,470,207.
27. Cone, J. H. (to Standard Oil Development Co.), U. S. Patent 2,426,082.
28. Kriger, J. J., *Coke and Chem. (U.S.S.R.)*, **1934,** No. 5–6, 91–3.
29. Dolbear, C. E. (to Industrial Research Corp.), U. S. Patent 1,440,973.
30. Borsig, A.-G. (Gustav Jansen, inventor), German Patent 520,120.
31. Heard, J. R., Jr. (to Wyandotte Chemicals Corp.), U. S. Patent 2,401,733.
32. Stanley, E., British Patent 374,437.
33. Mathias, H. R. (to Standard Oil Co. of Indiana), U. S. Patent 1,964,641.
34. Leviton, A., and Leighton, A., *J. Dairy Sci.*, **18,** 105 (1935).
35. Auclair, H. A., French Patent 845,543.
36. Meyer, E. A., and Distillers Co., Ltd., British Patent 349,288.
37. Horsfall, J. L., *J. Econ. Entomol.*, **27,** 259 (1934).
38. Zimmer, J. C., and McNulty, G. M. (to Standard Oil Development Co.), U. S. Patent 2,230,556.
39. Standard Oil Development Co., British Patent 560,810.
40. Standard Oil Development Co., French Patent 845,847.
41. Showalter, J. C. (to Standard Oil Development Co.), U. S. Patent 2,438,461.
42. Flaxman, M. T. (to Union Oil Co. of Calif.), U. S. Patent 2,127,491.
43. Zimmer, J. C. (to Standard Oil Development Co.), U. S. Patent 2,379,268.

44. Flaxman, M. T. (to Union Oil Co. of Calif.), U. S. Patent 2,127,490.
45. Thodos, G., and Weinaug, C. F. (to Phillips Petroleum Co.), U. S. Patent 2,449,427.
46. Fritz, J. H. (to National Oil Products Co.), U. S. Patent 2,304,304.
47. Fromm, R. (to Lehmann and Boss Co.), U. S. Patent 2,097,121.
48. Buch, A., and Lalleike, H. (to Chemische Fabrik Stockhausen Komm. Ges.), German Patent 715,109.
49. Thurman, B. H. (to Refining, Inc.), U. S. Patent 2,078,428.
50. Lubman, N. M., *Tsvetnye Met.*, No. 7–8, 28 (1932).
51. Segessemann, E. (to National Oil Products Co.), U. S. Patent 2,093,576.
52. Bue, H. E. (to Standard Oil Development Co.), U. S. Patent 2,052,164.
53. Bond, B. C., and Botsford (to Pure Oil Co.), U. S. Patent 2,349,585.
54. Fiske, C. H., *J. Biol. Chem.*, **35**, 411 (1918).
55. Iddings, C., and Kennedy, J. N. (to Muralo Co.), U. S. Patent 2,045,551.
56. Fritz, J. H. (to National Oil Products Co.), U. S. Patent 2,390,212.
57. Lighthipe, C. H. (to National Oil Products Co.), U. S. Patent 2,346,928.
58. Lighthipe, C. H. (to National Oil Products Co.), Canadian Patent 420,397.
59. Larsen, R. H. (to Fred Bresee, Jr.), U. S. Patent 2,412,276.
60. Modiano, F., *Bull. assoc. chim. sucr. dist.*, **50**, 445 (1933).
61. Fenske, M. R., and Cummings, G. H. (to Rhom and Haas Co.), U. S. Patent 2,407,954.
62. Bennett, H. T., and Marshall, J. R. (to Mid-Continent Petroleum Corp.), U. S. Patents 2,390,491–2.
63. Clapsadle, L. J. (to Carbide and Carbon Chemicals Corp.), U. S. Patent 2,298,465.
64. Brown, L. C. (to Industrial Patents Corp.), U. S. Patent 2,377,610.
65. Tribble, T. V. (to Flavor Corp. of America), U. S. Patent 2,508,978.
66. Hata, K., *J. Nippon Oil Technol. Soc.*, **1**, 28 (1948).
67. Nelson, R. C. (to Essential Oil Producers, Inc.), U. S. Patent 2,412,282.
68. Frey, C. N., and Miller, G. E. (to Standard Brands, Inc.), U. S. Patent 2,358,324.
69. Craig, D. (to B. F. Goodrich Co.), U. S. Patent 2,500,894.
70. Pacicot, P. A., and Ferguson, C. S., *Ind. Eng. Chem., Anal. Ed.*, **11**, 380 (1939).
71. *J. Assoc. Offic. Agri. Chemists*, **11**, 308 (1928).
72. Bernhard, A., *J. Am. Med. Assoc.*, **66**, 891 (1916).
73. Adoff, E. F., and Henderson, L. J., *J. Biol. Chem.*, **50**, 463 (1922).
74. Kennedy, R. K., *Paper Ind. and Paper World*, **20**, 1170 (1939).
75. Stolyarova, R. K., Russian Patent 45704.
76. Bocharov, *Tekhnika*, No. 111 (1935).
77. Steibelt, W., German Patent 602,087.
78. Tucker, W. M. (to Eastman Kodak Co.), U. S. Patent 2,147,415.
79. Ciba, Ltd., Swiss Patent 249,366.
80. Clarkson, R. G. (to E. I. duPont deNemours and Co.), U. S. Patent 1,981,635.
81. Richardson, R. W., and Schneider, R. B. (to E. I. duPont deNemours & Co.), U. S. Patent 1,981,634.

82. Schacht, F., G.m.b.H., German Patent 539,258.
83. Deutsche Hydrierwerke, A.-G. (S. Morgenstern, inventor), German Patent 642,103.
84. Chem. Fab. Stockhausen & Co., and Buch & Landauer, A.-G., German Patent 647,324.
85. Meyer, J. B., *Farben-Ztg.*, **36,** 41, 573, 619 (1930).
86. Steibert, —. (to I. G. Farbenind., A.-G.), U. S. Patent 2,085,709.
87. Borsoff, V. N., and Clayton, J. O. (to California Research Corp.), U.S. Patent 2,430,857.
88. Cellin, F., *Farbe u. Lack.*, **1938,** 461, 473.
89. Tremain, H. E., and Bacon, L. R. (to Wyandotte Chemicals Corp.), U. S. Patent 2,453,351.
90. Tremain, H. E., and Bacon, L. R. (to Wyandotte Chemicals Corp.), U. S. Patent 2,453,352.
91. Tremain, H. E., and Bacon, L. R. (to Wyandotte Chemicals Corp.), U. S. Patent 2,407,589.
92. *Petroleum Processing*, **2,** 907 (1947).
93. Reed, R. M. (to The Girdler Corp.), U. S. Patent 2,390,899.
94. Davis, O. L., and Nixon, A. C. (to Shell Development Co.), U. S. Patent 2,411,083.
95. Winning, C., Van Voorhies, R. L., and McNab, S. G. (to Standard Oil Development Co.), U. S. Patent 2,294,145.
96. Mannes, L., and Rummler, H. (to Henkel & Cie., G.m.b.H.), German Patent 700,677.
97. Lowenberg, K., Sattler, J., and Scholler, K. (to I. G. Farbenind., A.-G.), German Patent 704,862.
98. Borsoff, V. N., and Clayton, J. O. (to California Research Corp.), U. S. Patent 2,430,858.
99. Sokal, E. C., and Morris, R. C. (to Shell Development Co.), U. S. Patent 2,449,956.
100. Nixon, A. C., and Yabroff, D. L. (to Shell Development Co.), U. S. Patent 2,341,878.
101. Filbert, B. M. (to Standard Oil Development Co.), U. S. Patent 2,426,088.
102. Showalter, J. C. (to Standard Oil Development Co.), U. S. Patent 2,400,376.
103. Zhukhovitskii, Y., Azerbaĭdzhanskoe Neftyanoe Khoz., No. 4, 26 (1940).
104. Carlson, C. S., and Oakley, H. G. (to Standard Oil Development Co.), U. S. Patent 2,497,150.
105. Black, H. C. (to Industrial Patents Corp.), U. S. Patent 2,322,187.
106. Arroyo, R., *Sugar*, **43,** 31 (1948).
107. Rawling, R. G. (to West Virginia Pulp and Paper Co.), U. S. Patent 2,429,030.
108. Wolfson, J. (to National Oil Products Co.), U. S. Patent 1,957,513.
109. Wolfson, J. (to National Oil Products Co.), U. S. Patent 1,957,514.
110. Macarthur, A., and Stewart, A., British Patent 383,293.
111. Young, H. H., Jr. (to Industrial Patents Corp.), Canadian Patent 369,805.
112. Young, H. H., Jr. (to Industrial Patents Corp.), U. S. Patent 2,108, 912.

113. Macarthur, A., and Stewart, A. (to Imperial Chemical Industries, Ltd.), U. S. Patent 1,947,725.
114. Black, H. C. (to Industrial Patents Corp.), U. S. Patent 2,322,186.
115. Chemische Fabrik Grunau Landshoff and Meyer, A.-G., British Patent 361,094.
116. Zimmer, J. C. (to Standard Oil Development Co.), U. S. Patent 2,338,613.
117. Smith, H. G. (to Gulf Oil Corp.), U. S. Patent 2,377,654.
118. Barton, C. H., and Hughes, T. P. (to the Anglo-Saxon Petroleum Co., Ltd.), British Patent 564,281.
119. Osterloh, R. H., Pyle, C., Voitille, J. E., and Ficke, R. C. (to E. I. duPont deNemours and Co.), U. S. Patent 2,169,369.
120. Dyke, M., and Self, E. S. (to Oil Well Chemical and Materials Co., Inc.), U. S. Patent 2,475,485.
121. Retzsch, C. E., and Lighthipe, C. H. (to Nopco Chemical Co.), U. S. Patent 2,425,828.
122. Denman, W. L. (to Dearborn Chemical Co.), U. S. Patent 2,363,923.
123. Bird, P. G., and Jacoby, A. L. (to National Aluminate Corp.), U. S. Patent 2,428,776.
124. Denman, W. L. (to Dearborn Chemical Co.), U. S. Patent 2,304,805.
125. Denman, W. L. (to Dearborn Chemical Co.), U. S. Patent 2,400,543.
126. Imperial Chemical Industries, Ltd., British Patent 632,242.
127. Gunderson, L. O. (to Dearborn Chemical Co.), U. S. Patent 2,366,727.
128. Gunderson, L. O. (to Dearborn Chemical Co.), U. S. Patent 2,442,768.
129. Spellmeyer, E. F., U. S. Patent 1,892,857.
130. Imperial Chemical Industries, Ltd., British Patent 568,318.
131. Bird, P. G. (to National Aluminate Corp.), U. S. Patent 2,428,775.
132. Bird, P. G., and Jacoby, A. L. (to National Aluminate Corp.), Canadian Patent 433,431.
133. Imperial Chemical Industries, Ltd., British Patent 568,510.
134. Gunderson, L. O. (to Dearborn Chemical Co.), U. S. Patent 2,461,730.
135. Gunderson, L. O. (to Dearborn Chemical Co.), U. S. Patent 2,485,378.
136. Gunderson, L. O. (to Dearborn Chemical Co.), U. S. Patent 2,328,551.
137. Gunderson, L. O. (to Dearborn Chemical Co.), U. S. Patent 2,493,453.
138. Jacoby, A. L. (to National Aluminate Corp.), U. S. Patent 2,428,801.
139. Jacoby, A. L., and Bischmann, L. C., *Ind. Eng. Chem.*, **40**, 1360 (1948).
140. Jacoby, A. L., *J. Phys. & Colloid Chem.*, **52**, 689 (1948).
141. Bird, P. G., and Jacoby, A. L. (to National Aluminate Corp.), U. S. Patent 2,469,450.
142. Bird, P. G., and Jacoby, A. L. (to National Aluminate Corp.), U. S. Patent 2,481,899.
143. Ralston, A. W. (to Armour and Co.), U. S. Patent 2,168,847.
144. Kell, R. W. (to National Aluminate Corp.), U. S. Patent 2,449,656.
145. Böhme Fettchemie G.m.b.H., German Patent 707,877.
146. Böhme Fettchemie, G.m.b.H., German Patent 719,633.
147. Flett, L. H. (to National Aniline & Chemical Corp.), U. S. Patent 2,074,380.
148. Johnson, H. G. (to Commercial Solvents Corp.), U. S. Patent 2,433,825.

149. Fritz, J. H., and Robinson, E. A. (to National Oil Products Co.), U. S. Patent 2,347,178.
150. Monson, L. T. (to Petrolite Corp., Ltd.), U. S. Patent 2,408,527.
151. Smith, H. G., and Cantrell, T. L. (to Gulf Oil Corp.), U. S. Patent 2,452,693.
152. Batchelder, A. H., and Rollins, F. S., Jr. (to California Research Corp.), U. S. Patent 2,402,487.
153. Zimmer, J. C., and Seitz, W. (to Standard Oil Development Co.), U. S. Patent 2,355,255.
154. Smith, H. G., and Cantrell, T. L. (to Gulf Oil Corp.), U. S. Patent 2,408,232.
155. Smith, H. G., Cantrell, T. L., and Hill, M. L. (to Gulf Oil Corp.), U. S. Patent 2,447,288.
156. Smith, H. G., and Cantrell, T. L. (to Gulf Oil Corp.), U. S. Patent 2,397,377.
157. Smith, H. G., and Cantrell, T. L. (to Gulf Oil Corp.), U. S. Patent 2,397,378.
158. Smith, H. G., and Cantrell, T. L. (to Gulf Oil Corp.), U. S. Patent 2,397,379.
159. Smith, H. G., and Cantrell, T. L. (to Gulf Oil Corp.), U. S. Patent 2,397,380.
160. Smith, H. G., and Cantrell, T. L. (to Gulf Oil Corp.), U. S. Patent 2,397,381.
161. Smith, H. G., and Cantrell, T. L. (to Gulf Oil Corp.), U. S. Patent 2,411,671.
162. Rell, C. N. (to Socony Vacuum Oil Co.), U. S. Patent 2,353,587.
163. Sandoz, Ltd., Swiss Patent 236,679.
164. Brodersen, K., and Quaedvlieg (to I. G. Farbenind., A.-G.), German Patent 724,755.
165. Ross, S., and McBain, J. W., *Ind. Eng. Chem.*, **36**, 570 (1944).
166. I. G. Farbenindust., A.-G., British Patent 526,690.
167. Brodersen, K., and Quaedvlieg, M. (to I. G. Farbenind., A.-G.), U. S. Patent 2,220,485.
168. Larsen, R. G., and Diamond, H. (to Shell Development Co.), U. S. Patent 2,375,007.
169. Ambrose, A. J., and Trautman, C. E. (to Gulf Research and Development Co.), U. S. Patent 2,416,503.
170. Ambrose, A. J., and Trautman, C. E. (to Gulf Research and Development Co.), U. S. Patent 2,416,504.
171. Bollinger, L. C. (to Shell Development Co.), U. S. Patent 2,435,124.
172. Trautman, C. E., *Lubricating Eng.*, **2**, 143 (1946).
173. Zimmer, J. C., and Duncan, G. W. (to Standard Oil Development Co.), U. S. Patent 2,444,970.
174. Hersh, J. M. (to Continental Oil Co.), U. S. Patent 2,464,231.
175. Diamond, H. (to Shell Development Co.), U. S. Patent 2,406,671.
176. Vail, J. H., *Anal. Chem.*, **19**, 506 (1947).
177. Coppock, P. D., and The Distillers Company, Ltd., British Patent 639,507.
177a. Currie, C. C., and Dow Corning Corp., British Patent 639,673.

178. Standard Oil Development Co., British Patent 614,626.
179. Walker, H. W., and Morrow, R. W. (to E. I. duPont deNemours and Co.), U. S. Patent 2,482,307.
180. Scott, R. B., Jr. (to E. I. duPont de Nemours and Co.), U. S. Patent 2,462,999.
181. Ciba, Ltd., Swiss Patent 257,713.
182. Dow Corning Corp., British Patent 630,952.
183. Trautman, C. E. (to Gulf Research and Development Co.), U. S. Patent 2,515,024.
184. Trautman, C. E. (to Gulf Research and Development Co.), U. S. Patent 2,488,449.
185. Trautman, C. E., and Ambrose, H. A. (to Gulf Research and Development Co.), U. S. Patent 2,416,360.
186. Evans, E. A., and Elliott, J. S. (to C. C. Wakefield and Co., Ltd.), British Patent 596,150.
187. Hartough, H. D., and Kosak, A. I. (to Socony Vacuum Oil Co., Inc.), U. S. Patent 2,478,484.
188. Nixon, A. C., and Yabroff, D. L. (to Shell Development Co.), U. S. Patent 2,411,105.
189. Ralston, A. W. (to Armour and Co.), U. S. Patent 2,101,560.
190. Bradshaw, L., U. S. Patent 1,833,771.
190a. Bradshaw, L., U. S. Patent 1,833,772.
191. Denman, W. L. (to Dearborn Chemical Co., Inc.), U. S. Patent 2,439,797.
192. Rosen, R., and Zimmer, J. C. (to Standard Oil Development Co.), U. S. Patent 2,440,489.
193. Zimmer, J. C., and Rosen, R. (to Standard Oil Development Co.), U. S. Patent 2,449,631.
194. Davis, G. H. B., and Zimmer, J. C. (to Standard Oil Development Co.), U. S. Patent 2,435,205.
195. Davis, G. H. B., and Zimmer, J. C. (to Standard Oil Development Co.), U. S. Patent 2,435,206.
196. Davis, G. H. B., and Zimmer, J. C. (to Standard Oil Development Co.), U. S. Patent 2,394,596.
197. Davis, G. H. B., and Zimmer, J. C. (to Standard Oil Development Co.), U. S. Patent 2,515,115.
198. Fronmuller, D., and Boyles, F. M. (to Coffee Products Corp.), U. S. Patent 2,118,184.
199. Denman, W. L. (to Dearborn Chemical Co.), U. S. Patent 2,363,924.
200. Craig, D. (to The B. F. Goodrich Co.), U. S. Patent 2,432,386.
201. Tyrer, D., U. S. Patent 2,452,404.
202. Anon, *Chem.-Ztg.*, **59**, 857 (1935).
203. Karasik, P. I., and Dobashkin, V. I., Russian Patent 51,921.
204. DeCew, J. A. (to Process Engineers, Inc.), U. S. Patent 1,573,814.
205. Gunderson, L. O. (to Dearborn Chemical Co.), U. S. Patent 2,391,895.
206. Hill, E. F. (to Wyandotte Chemicals Corp.), U. S. Patent 2,359,913.
207. Holmes, J. A., *Power*, **75**, 241 (1932).
208. Carrick, O. W., *J. Am. Water Works Assoc.*, **9**, 906 (1922).
209. Dreyfus, C., and Haney, C. I. (to Celanese Corp. of America), U. S. Patent 1,936,754.

210. Clapsadle, L. J. (to Carbide and Carbon Chemicals Corp.), U. S. Patent 1,899,610.
211. Neumann, S., and F. W. Beck and Co., Ltd., British Patent 580,620.
212. Becker, J. (to Koppers Co.), U. S. Patent 1,756,234.
213. Denman, W. L. (to Dearborn Chemical Co.), U. S. Patent 2,439,797.
214. Mack, J., *Przemysl Naftowy*, **12**, 177 (1937).
215. Hall, R. E., U. S. Patent 1,759,615.
215a. Spencer, G. L., and Meade, G. P., "Cane Sugar Handbook," 8th ed., New York, J. Wiley & Sons, 1945.
216. Cohen, C., *Sewage Works J.*, **1**, 58 (1928).
217. Cohen, C., *Eng. News Record*, **98**, 563 (1927).
218. Luisada, A. A., *Proc. Soc. Exptl. Biol. Med.*, **74**, 215 (1950).
219. Rafton, H. R. (to Raffold Process Corp.), U. S. Patent 1,831,928.
220. National Aluminate Corp., British Patent 451,929.
221. Denman, W. L. (to Dearborn Chemical Co.), U. S. Patent 2,439,797.
222. Solberg, T. A., U. S. Patent 2,097,649.
223. Esch, W., *Gelatine, Leim, Klebstoffe*, **2**, 51 (1934).
224. Swenson, T. L. (to People of the U.S.A. for free use), U. S. Patent 2,110,613.
225. Bendien, W. M., *Chem. Weekblad*, **33**, 547 (1936).
226. Anon, *Farben-Ztg.*, **26**, 2291 (1921).
227. French, D. K., *Ind. Eng. Chem.*, **26**, 1319 (1934).
228. "Esters by Glyco," Glyco Products Co., Inc.
229. Dollinger, J. H., Private Communication.
230. "Atlas Surface Active Agents," Atlas Powder Co.
231. Abbott, W. K., Private Communication.
232. "Nalco Paper Mill Antifoam," May 1950, National Aluminate Corp.
233. Technical Data Sheet, Nov. 1, 1951, National Aluminate Corp.
234. Technical Data Sheet, Nov. 1, 1951, National Aluminate Corp.
235. Technical Data Sheet, El Dorado Oil Works.
236. Cupples, R. L., Private Communication.
237. Technical Data Sheet M-211, Dearborn Chemical Co.
238. Gunderson, L. O., Private Communication.
239. Gunderson, L. O., and Bodach, C. M., Paper presented at the Midwest Power Conference, April 1951.
240. "Polyamide Antifoam Treatments," Dearborn Chemical Co.
241. Technical Data Sheet, Nov. 1, 1950, National Aluminate Corp.
242. Blume, P. W., Private Communication.
243. "Ucon Brand Fluids and Lubricants," Carbide and Carbon Chemicals Division, Union Carbide and Carbon Corp.
244. Technical Bulletin No. P-140, Monsanto Chemical Co.
245. Benignus, P. G., Private Communication.
246. "Synthetic Organic Chemicals," Carbide and Carbon Chemicals Corp.
247. "DC Antifoam A," Dow Corning Corp.
248. Rowe, V. K., Spencer, H. C., and Bass, S. L., *J. Ind. Hyg. Toxicol.*, **30**, 332 (1948).
249. Rowe, V. K., Spencer, H. C., and Bass, S. L., *Arch. Ind. Hyg. and Occupational Med.*, **1**, 539 (1950).

250. Clark, L. C., Gollan, F., and Gupta, V. B., *Sciences*, **111,** 85 (1950).
251. Goldschmidt, M. E., and Koffler, H., *Ind. Eng. Chem.*, **42,** 1819 (1950).
252. "The Use of G.E. Silicones in Defoaming," General Electric Co.
253. "Silicone Antifoam Agent," General Electric Co.
254. Special Technical Bulletin, Wyandotte Chemicals Corp.
255. Technical Data Sheet, Sept. 1950, Hercules Powder Co.
256. Technical Data Sheet, Glyco Products Co., Inc.
257. Technical Data Sheet No. 7, Commercial Solvents Corp.
258. Technical Data Sheet, E. F. Drew and Co., Inc.

AUTHOR INDEX

Abbott, J. A., 289, 296
Abbott, W. K., 315, 328
Abramchuk, N. A., 80, 96
Abribat, M., 171, 182
Achorn, G. B., 9, 25
Adams, G. L., 262, 276
Adams, J. C., 13, 14, 26
Addison, C. C., 163, 170
Ader, J., 135, 136
Adoff, E. F., 303, 323
Aero Research, Ltd., 285, 295
A. G. für technische Neuheiten, 237, 242
Aenlle, E. O., 178, 182
Aldinger, W., 44, 49, 80, 95
Aleinikov, N. A., 34, 38, 45, 46, 47, 48, 55, 57, 58, 63, 76, 93, 95, 117, 135
Alejnikoff. *See* Aleinikov
Aluminum Co. of America, 269, 279
Ambrose, A. J., 309, 326
Ambrose, H. A., 310, 327
Amdyco Corp., 222, 240
American Agricultural Chemical Co., 246, 272, 279
American Cyanamid Co., 244, 246, 257, 258, 261, 268, 269, 271–281
American Fomon Co., 222, 240
American-La France Foamite Corp., 215, 218, 239
American Potash and Chemical Corp., 273, 281
Amerine, M. A., 109, 113
Amsel, O., 203–205, 207, 210, 238
Anderson, A. W., 246, 272, 278
Anderson, C. O., 269, 279
Anderson, L. D., 273, 281
Anderson, O. F., 299, 321
Anderson, R. A., 9, 25
Andrews, G., 181, 183
Anglo-Saxon Petroleum Co., Ltd., 306, 325
Antignit Gesellschafft, Ltd., 218, 239
Arbuzov, K. N., 100, 101, 103, 108, 112
Arca-Regler, A. G., 294, 296
Armour and Co., 232, 241, 246, 261, 262, 271, 272, 276–279, 308, 311, 325, 327
Arrazola, J. M., 171, 182
Arroyo, R., 305, 324
Atlas Powder Co., 315, 328
Auclair, H. A., 300, 322
Austin, R. W., 221, 240
Australasian Institute of Mining and Metallurgy, 244, 274

Bachmann, F., 98, 108, 109, 112
Bacon, C. C., 300, 322
Bacon, L. R., 304, 324
Bader, R., 78, 95, 176, 179, 181–183
Badger Fire Extinguisher Co., 218, 239
Bagley, T. J., 230, 241
Bailey, M. I., 41, 49, 99, 114–116, 135
Bailey, O. T., 291, 296
Baldacci, R., 72, 91, 94
Ballot, J., 245, 274
Barber, E. G., 299, 322
Barber Asphalt Paving Co., 262, 276
Barbour, A. D., 38, 41, 48, 114–116, 135
Barbre, C., 262, 276
Barkley, J. E., 27, 28, 32, 47, 50, 93
Barmore, M. A., 102, 110, 112, 114, 116, 135, 174, 182, 286, 295
Barr, J. A., 246, 271, 279
Barrett Co., 262, 276
Bartels, E., 214, 239
Barti, P., 299, 322
Bartsch, O., 54, 55, 57, 58, 61, 62, 75, 85, 91, 93, 166, 167, 170, 186–188
Basic Magnesium, Inc., 269, 278
Bass, S. L., 319, 328
Barton, C. H., 306, 325
Batchelder, A. H., 308, 326
Bateman, J. B., 11, 26
Bates, W. A., 246, 252, 255, 261, 269, 271, 275, 276, 278, 279
Bashforth, F., 13, 14, 26
Baumann, A., 180, 182
Beeching, E. I., 286, 295
Beek, F. W., and Co., 312, 328
Becker, J., 312, 328
Belani, E., 300, 303, 322
Bell, R. W., 129, 136
Bendien, W. M., 313, 328
Benignus, P. G., 318, 328
Bennett, H. T., 302, 323
Bennion, E. B., 91, 97
Benson, C. C., 173, 182
E. Berghausen Chemical Co., 222, 240
Berghausen, A., 222, 240
Bering, E. A., 291, 296
Berkman, S., 90, 97
Bernhard, A., 303, 323
Bertsch, H., 225, 241
Beythein, R., 222, 240
Biddle, A., 217, 239
Bikerman, J. J., 2, 9, 16, 22, 25, 26, 29, 30, 34, 36, 37, 47, 48, 52, 54, 63, 72, 93, 94, 106, 113, 123, 124, 132, 135, 136, 146, 150, 154, 155, 157, 163, 169, 170
Bird, P. G., 306–308, 325
Bischmann, L. C., 18, 26, 307, 325
Bishop, W. T., 254, 259–261, 275, 276
Bissel, W. H., 261, 276
Black, H. C., 83, 96, 305, 324, 325
Black, J. C., 215, 239
Blackman, M., 90, 96, 121, 129, 135, 136, 144
Blakeborough, R. A., 218, 239
Blenio, G., 218, 239
Blom, J., 103, 109, 112
Blume, P. W., 317, 320, 328
Bocharov, 303, 323
Bodach, C. M., 85, 96, 317, 328
Bogue, R. H., 78, 95
Böhme Fettchemie-Gesellschaft m. b. H., 225, 241, 308, 325
Böhme, H. Th., 220, 238, 239, 242
Bollinger, L. C., 309, 326
Bolton, E. K., 245, 275
Bond, B. C., 301, 323
Bondarenko, A. N., 44, 49, 91, 97
Bonneville, Ltd., 246, 273, 280
Booth, R. B., 244, 246, 271, 274, 279, 280
Borcherdt, W. O., 269, 279
Borsig, A.-G., 300, 322
Borsoff, V. N., 304, 324
Botsford, 301, 323
Boyd, F. L., 198, 199, 218, 239
Boyles, F. M., 312, 327
Boys, C. V., 150
Bradshaw, L., 311, 327
Brady, A. P., 44, 45, 47, 49, 81, 83, 91, 96, 103, 105, 106, 110, 112, 169, 170, 177, 182
Bragg, L., 8, 25, 68, 94
Bransky, D. W., 284, 295
Breerwood, C. H., 268, 277
Breitner, H. J., 88, 96
Brennan, J. H., 269, 279

Brenner, M. W., 99, 104, 112, 116, 135
Bresee, Fred., 302, 323
Bresler, S. E., 80, 96
Brill, H. C., 188
British Dyestuffs Corp., 220, 239
Broadbridge, W., 246, 269, 272, 278
Brockmann, C., 91, 97
Brodersen, K., 309, 326
Brown, A. G., 78, 79, 80, 95
Brown, E. H., 271, 279
Brown, J. C., 237, 242
Brown, L. C., 302, 323
Bruckner, F., 123, 294, 296
Brunner, K., 300, 322
Brunswig, 207, 238
Bubblestone Co., 289, 295
Bue, H. E., 301, 323
Buch, A., 300, 322
Buch & Landauer A. G., 303, 324
Burcik, E. J., 63, 64, 68, 94, 160, 165, 169
Burgess, L., 220, 239
Burmeister, H., 221, 240
Burwell, B., 269, 279
Busse, W. F., 231–233, 241
Byrnes, C. P., 262, 276

Cahn, F. J., 246, 272, 278
California Research Corp., 246, 261, 271, 276, 279, 304, 308, 324, 326
Callow, J. M., 264, 277
Campbell, B., 80, 96
Campbell, T. P., 273, 281
Cannon, H., 262, 276
Cantrell, T. L., 308, 309, 326
Carbide and Carbon Chemicals Corp., 259, 275, 300, 302, 312, 318, 319, 322, 323, 328
Carnahan, T. S., 262, 276
Carlson, C. S., 305, 324
Carpentier, P. J., 290, 296
Carrell, C. J., 284, 295
Carriek, O. W., 312, 327
Cattermole, A. E., 245, 274
Celanese Corp. of America, 312, 327
Cellin, F., 304, 324
Central Soya Co., 287, 295
Chaminade, R., 134–136
Chapman, E., 220, 239
Chappell, M. L., 215, 239
Chatalan, J., 172, 174, 182
Chemical Concentrates Corp., 230, 241
Chemical Construction Corp., 244, 274, 281
Chemische Fabrik Grunau, Landshoff and Meyer, 305, 325
Chemische Fabrik Stockhausen Komm.-Ges. & Co., 300, 301, 303, 322–324
Christensen, N. C., 246, 281
Christmann, L. J., 246, 252, 257, 258, 268, 269, 272, 275, 276, 278, 281
Ciba, Ltd., 303, 310, 323, 327
Clapsadle, L. J., 302, 312, 323, 328
Clark, C. L., 319, 329
Clark, G. L., 34, 48, 80, 89, 95, 103, 112, 180
Clark, N. O., 38, 40, 48, 79, 90, 95, 96, 114, 121, 125, 126, 135, 144, 148, 150, 169, 170, 200–205, 207–210, 212, 236, 238, 242
Clark, T., 292
Clarkson, R. G., 303, 323
Clayton, J. O., 304, 324
Clemmer, J. B., 269, 271, 279
Clemmons, B. M., 269, 271, 279
Clevenger, G. H., 262, 276
Coffee Products Corp., 312, 327
Cohen, C., 313, 328
Coke, H. W., 262, 277
Cole, A. T., 246, 272, 273, 280
Combustion Utilities Corp., 258, 275
Commercial Solvents Corp., 308, 321, 325, 329
Cone, J. M., 300, 322
Constable, F. H., 43, 49, 115, 135
Continental Oil Co., 309, 326
Cook, G. A., 68, 94
Cooper, K. W., 11, 26
Coppock, P. D., 3–5, 25, 310, 326
Corley, H. M., 246, 272, 278
Cornwell, E. D., 285, 295
Corson, B. I., 221, 240
Courrier, R., 181, 183
Crago, A., 246, 269, 272
Craig, D., 303, 312, 323, 327
Crosby, P. A., 215, 239
Cummings, G. H., 302, 323
Cunningham, O. D., 258, 275
Cupples, R. L., 316, 328
Curric, C. C., 310, 326

Dachlauer, K., 224, 240
Dailey, J. P., 231, 241
Daimler, K., 199, 220, 227, 228, 236, 239, 241, 242
Datta, R. L., 3, 4, 25
Davis, G., 236, 242
Davis, G. H. B., 311, 312, 327
Davis, O. L., 304, 324
Davis, S. C., 180, 182
Davis, T. L., 285, 295
Day, H. M., 246, 268, 272, 277, 278
Dean, R. B., 11, 12, 26
Dean, R. S., 71, 94
Dearborn Chemical Co., 306, 307, 311–313, 317, 325, 327, 328
De Bruyne, N. A., 285, 295
Debye, P. P., 232, 241
DeCew, J. A., 312, 327
Dedrick, C. H., 67, 94
Defense Plant Corp., 269, 278
Delprat, G. D., 245, 274
DeLue, 12
De Mattei, W., 109, 113
Denman, W. L., 18, 26, 43, 49, 306, 307, 311–313, 325, 327, 328
Denton, G. P., 289, 296
Denuelle, P., 83, 96
Derjaguin. *See* Deryagin
Deryagin, B., 118, 119, 124–126, 129, 135, 136
Desch, C. H., 25, 26, 89, 96
Dessèvre, J., 273, 281
Deutsche Gold- und Silber-Scheideanstalt vormals Roessler, 262, 276
Deutsche Hydrierwerke A. G., 303, 324
De Vaney, F. D., 271, 279
Dewar, J., 31, 48, 68, 94, 120, 121, 127, 132, 135, 136, 156, 157, 294, 296
Diamond, H., 310, 326
Dierkes, H., 41, 49
Dieterle, R., 83, 96
Distillers Co., Ltd., 300, 310, 322, 326
Dittus, F. W., 219, 239
Diwoky F. F., 284, 295
Dobashkin, V. I., 312, 327
Doerner, H. A., 269, 278
Dognon, A., 171, 181–183
Dolbear, C. E., 300, 322
Dole, R. A., 291, 296
Dollinger, J. H., 315, 328
Dollman, D. Y., 198, 200, 238
Donnan, F. G., 167, 170
Dörfeldt, W., 179, 182
Douglas, W. A., 246, 275
Dow Chemical Co., 250, 252, 257, 273, 275, 281
Dow Corning Corp., 310, 319, 326–328
Dreger, E. E., 70, 94
Drew, E. F., and Co., 321, 329
Dreyfus, C., 312, 327
Drouot, P., 176, 182
Drude, P., 143, 144 152, 153, 157
Dubrisay, R., 176–178, 182, 291, 296
Duke, J. B., 246, 272, 273, 278, 280

Dumanskii, A. V., 39, 48, 76, 80, 89, 90, 95
Duncan, G. W., 309, 326
Duncan, W. E., 269, 279
Dunlap, F. L., 221, 222, 240
Du Pont de Nemours and Co., 245, 246, 259, 261, 262, 272, 273, 275–278, 280, 281, 300, 303, 306, 310, 322, 323, 325, 327
Dupré A, 120, 132–136
Durney, H. A., 168, 170
Durov, S. A., 43, 49, 52, 93, 188
Dyakonov, G. K., 36, 37, 48
Dyke, M., 306, 325

Eastman Kodak Co., 303, 323
Eberle, C., 42, 49
Eckelmann, L. E., 221, 240
Edgar Brothers Co., 262, 277
Edgar Plastic Kaolin Co., 272, 280
Edser, E., 246, 262, 269, 272, 278
Egloff, G., 90, 97
Eguchi, G. M., 243, 274
Eisele, J., 262, 276
El Dorado Oil Works, 316, 328
Elkonin, N. V., 109, 113
Ellehammer, 189, 238
Elliott, J. S., 311, 327
Elliott, T. A., 163, 170
Ellis, E. E., 262, 277
Elmore, A. S., 245, 274
Elmore, F. E., 245, 274
El-Rafey, M. S., 91, 97
Emulsol Corp., 246, 262, 272, 277, 278
Epstein, A. K., 262, 277
Erbring, C., 103, 109, 112
Erickson, S. E., 246, 268, 269, 272, 277, 278
Ericson, R., 289, 296
Erie Mining Co., 271, 279
Erkut, H., 43, 49
Ermolenko, N. F., 80, 96
Erwin, J. B., 213, 238
Erwin, O. R., 213, 238
Esch, W., 313, 328
Esselen, G. J., 218, 239
Esselen, W. B., 180, 182
Essential Oil Producers, Inc., 302, 323
Estes, C., 180, 183
Evans, E. A., 311, 327
Evans, R. D., 246, 272, 278
Evans, R. W., 89, 96
Evans, T. W., 300, 322
Eversole, W. G., 6, 25
Ewer, B. T., 221, 222, 240
Excelsior Feuerlöschgeräte, A.-G., 222, 240

Faber, L. D., 284, 295
Faber Engineering Co., 284, 295
Fabrike Chemischer Prop., 225, 241
Fahrenwald, A. W., 269, 278
Fairley, T. J., 218, 239
Fellers, C. R., 180, 182
Fenske, M. R., 302, 323
Ferguson, C. S., 302, 323
Ferguson, G. E., 218, 221, 239, 240
Fernandez, S. G., 178, 182
Fesenko, N. G., 52, 93
Fiero, G. W., 67, 94
Ficke, R. C., 306, 325
Fife, H. R., 300, 322
Filbert, B. M., 305, 324
Fischer, A. H., 246, 275
Fisher, G. M., 282, 294
Fiske, C. H., 90, 96, 301, 323
Flavor Corp. of America, 302, 323
Flaxman, M. T., 301, 322, 323
Flett, L. H., 308, 325
Ford, W. D., 288, 295
Foulk, C. W., 27, 28, 32, 33, 47, 48, 50, 52, 93, 169, 170, 187, 188, 205, 299, 321
Fourt, L., 159, 169
Forrest, C. N., 262, 276
Forrester, D. W., 265, 277
Fox, J. H., 288, 295
Frederick, H. E., 261, 276
Freeport Sulphur Co., 262, 277
Frelat, M., 71, 94
French, D. K., 299, 313, 321, 328
French, R. J., 10, 26, 207, 208, 238
Frey, C. N., 302, 323
Friedel, G., 156, 157
Friedrich, K., 200, 203, 207, 210, 228, 238, 241
Fritz, J. H., 301, 302, 308, 323, 326
Fromm, R., 301, 323
Fronmuller, D., 312, 327
Frumkin, A., 15, 17, 26
Fry, J. F., 10, 26, 207, 208, 238
Fuchs, E., 222, 240
Fyr-Fyter Co., 215, 220, 239, 240

Gallai-Hatchard, M., 289, 296
Ganelina, S. G., 84, 96
Garratt, W. R., 218, 239
Garrett, B. S., 300, 322
Gastrock, E. A., 134, 136
Gaudin, A. M., 34, 48, 63, 94, 243, 244, 250, 274
Gaylor, P. J., 262, 277
General Aniline Works, 220, 231, 239, 241
General Electric Co., 319, 329
General Petroleum Corp., 262, 276
Gernez, D., 12, 26
Geys, K., 180, 182
Gibb, W., 54, 55, 61, 93
Gibbs, J. W., 23, 105, 113, 160, 162, 167, 168
Gieseke, E. W., 246, 269, 272, 278, 279
Gilberg, D., 9, 25
Gillson, J. L., 262, 277
Girdler Corp., 304, 324
Gleim, V. G., 299, 322
Glyco Products Co., Inc., 313, 320, 328, 329
Godbole, N. N., 107, 113
Goldschmidt, M. E., 319, 329
Gollan, F., 319, 329
Gooderham, W. J., 293, 296
Goodner, E. F., 219, 220, 239, 240
Goodrich, B. F., Co., 303, 312, 323, 327
Götte, E., 40, 41, 49, 64, 65, 69, 70, 71, 94
Goyden, G. A., 245, 274
Granskaya, T. A., 76, 80, 89, 90, 95
Grasselli Chemical Co., 262, 277
Gray, P. P., 108, 109, 113–116, 135, 171, 180, 182
Grebenshchikov, B. N., 100 101, 103, 108
Greeman, O. W., 269, 279
Greene, E. W., 246, 272, 273, 278, 280
Greenway, H. H., 245, 258, 274, 275
Gregory, G. A., 215, 239
Griessbach, R., 262, 276
Gross, 225, 240
Grove, C. S., 130, 136, 205, 238
Guggenheim Brothers, 246, 275
Gulf Oil Corp., 306, 308, 309, 325, 326
Gulf Research and Development Co., 309, 310, 326, 327
Gulf States Paper Co., 262, 277
Gunderson, L. O., 18, 26, 43, 49, 85, 96, 306, 307, 312, 317, 325, 327
Gunther, F. C., 12, 26
Gupta, V. B., 319, 329
Guthke, W. F., 220, 240
Guyer, A., 3–6, 25
Gvirtsman, N., 77, 95

Haacke, 299, 322
Hackford, J. E., 39, 48, 80, 91, 95
Hadorn, H., 80, 95
Haefele, C. R., 59, 94
Haefly, H., 285, 295

Hagenbach, A., 146, 147, 150, 153, 154, 157
Hall, R. E., 313, 329
Hammes, H., 17, 26
Hancock, J. S., 47, 49, 52, 93
Hancock, Th., 290
Handy, R. S., 262, 277
Haney, C. J., 312, 327
Hansen, M. S., 256, 275
Hardenbergh, W. A., 284, 295
Hardy, W. B., 32, 48, 72, 94
Harkins, W. D., 159, 169
Harreis, F., 180, 182
Harris, B. J., 273, 281
Harris, B. R., 262, 272, 280, 281
Harris, D. L., 269, 278
Hartner-Seberich, R., 83, 96
Hartough, H. D., 311, 327
Harvey, E. N., 11, 26, 188
Harwood, J., 246, 261, 272, 276, 278
Hasselstrom, T., 262, 277
Hata, K., 302, 323
Hatschek, E., 130, 136
Hawaiian Pincapple Co., Ltd., 243, 274
Hawthorne, J. R., 91, 97
Hay, R. L., 116, 135
Hazel, F., 38, 48, 79, 84, 95, 171, 180, 182, 197, 231, 238, 241
Hazlehurst, T. H., 32, 48, 168, 170
Head, C. W., 246, 269, 272, 278
Heard, J. R., 300, 322
Heilman, T., 268, 277
Helm, E., 40, 48, 91, 97, 98, 109, 110, 112
Henderson, L. J., 303, 323
Henkel and Cie., 237, 242, 304, 324
Henry, W. C., 38, 41, 48, 114, 115, 116, 135
Hercules Powder Co., 259–262, 275–277, 320, 329
Herkenhoff, E. C., 246, 271, 279
Herrly, C. J., 259, 275
Herry, G. J., 261, 276
Hersberger, A. B., 71, 94
Hersh, J. M., 309, 326
Hetzer, 40, 48, 107, 113
Heuck, C., 262, 276
Higgins, A. H., 245, 262, 274, 277
Hill, E. F., 312, 327
Hill, E. G., 256, 275
Hill, M. L., 308, 326
Hills, C., 232, 241
Hills, R. C., 262, 277
Hoag, E. H., 269, 279
Hochwalt, C. A., 215, 220, 239
Hodges, P., 262, 277
Hoftijzer, P. J., 3, 6, 7, 25
R. M. Hollingshead Corp., 230, 241
Hollingsworth, C. A., 246, 272, 278
Holmes, J. A., 312, 327
Holter, C. B., 220, 240
Holwerda, K., 78, 95
Hood, O. E., and M., 225, 241
Horiuchi, R., 75, 95
Horliek, Ltd., 286, 295
Horsfall, J. L., 300, 322
Houston, W. M., 246, 272, 273 278, 280
Houwink, R., 285, 295
Htin, K., 54, 55, 61, 93
Hubbard, D. A., 285, 295
Hughes, T. P., 306, 325
Hunter, M. P., 218, 239
Hunter, W. J., 218, 239

Iddings, C., 302, 323
I. G. Farbenindustrie A.-G., 220, 229, 236, 237, 240, 241, 262, 276, 304, 309, 324, 326
Imperial Chemical Industries, Ltd., 236, 241, 307, 325
Ince, C. R., 75, 95, 251, 275
Industrial Patents Corp., 302, 305, 323, 324
Industrial Research Corp., 300, 322
Ingraham, F. D., 291, 296
Ingraham, J. S., 232, 241
Institute of Paper Chemistry, 300, 322
International Minerals & Chemical Corp., 273, 280
International Smelting and Refining Co., 247, 281
Isemura, T., 74, 94

Jackson, R. I., 273, 280
Jacobsen, W. B., 273, 281
Jacoby, A. L., 18, 26, 307, 308, 325
Jakob, M., 12, 15–17, 26
James, J. H., 262, 276
Janney, T. A., 245, 275
Jansen, G., 300, 322
Jayne, D. W., Jr., 246, 252, 258, 268, 269, 272, 275–278
Jenckel, E., 17, 26
Jennings, J. M., 223, 240
Johlin, J. M., 66, 94
Johnson, H. G., 308, 325
Johnston, F. F., 246, 269, 272, 278
Johnston, N. F., 286, 295
Johonnot, E. S., 152, 153, 157
Joly, M., 159, 169
Jones, 222, 240

Kabanov, B., 15, 17, 26
Kapitańczyk, K., 11, 26
Karasik, P. I., 312, 327
Karreth, A., 283, 294
Kasyanova, N., 77, 95
Katzman, M., 246, 262, 272, 277. 278
Kauffmann, F. L., 291, 296
Kaufmann, H. P., 100, 110, 112
Keil, F., 96, 232, 241
Keil, H. L., 232, 241
Kell, R. W., 308, 325
Keller, C. H., 245, 275
Kennedy, J. N., 302, 323
Kennedy, R. K., 303, 323
Kennedy, R. N., 290, 296
Kent, G., 220, 239
Kharin, S., 90, 96, 300, 322
Kind, W., 77, 95
King, E. G., 83, 96, 116, 135
King, G. D., 289, 295
Kionka, H., 44, 49
Kitaigorodskii, I. I., 288. 295
Kirby, J. E., 246, 261, 273, 276, 280
Kirk, M. W., 273, 281
Kirkpatriek-Pieard, H. F., 245, 274
Kirseh, P., 100, 110, 112
Kirstahler, 237, 242
Kishi, Y., 75, 95
Klees, A. L., 258, 275
Kodak-Pathé, 130, 136, 291, 292, 296
Koffler, H., 319, 329
Kollmann, L., 43, 49
Komet Kompagnie, 189, 238
Koppers Co., 312, 328
Kosak, A. I., 311, 327
Kovalski, W. v., 3, 25
Krause, A., 11, 26
Krauss, G., 180, 182
Kreidl, E. L., 228, 295
Krevelen, D. W., van, 3, 6, 7, 25
Kriger, J. J., 300, 322
Kritchevsky, W., 246, 272, 278
Krzikalla, H., 220, 240
Kubota, H., 139, 144
Kuehner, A. L., 68, 94
Kuzin, S. A., 117, 135

Lafforge, J. W., 269, 278
Laing, M. E., 175, 182
Lallcike, H., 300, 301, 322, 323
Lamberg, J. M., 232, 241
Landolt, G. L., 256, 275
Lane, G. J., 262, 277
Lang, J., 11, 26
Laplace, 10, 12, 15, 19, 131, 151, 294

Larsen, R. H., 302, 309, 323, 326
Larson, R. F., 12, 26
Laufer, S., 93, 104, 110, 112, 113, 116, 135
Laughton, E., 245, 274
Laurent, 189, 213, 238
Leaf, W. B., 16, 26, 42, 43, 49, 51, 52, 93, 188
Learmonth, E. M., 286, 295
Lederer, E. L., 38, 48, 67, 94, 103, 107, 111, 112, 113
Lee, S., 174, 182
Lehmann and Boss Co., 301, 323
Leighton, A., 300, 322
Lenderink, J., 287, 295
Lenhart, W. B., 273, 280
Lenher, S., 246, 262, 277, 281
Leslie, E. H., 262, 276
Lessels, V., 247, 281
Levin, D., 230, 241
Leviton, A., 300, 322
Lewis, C. P., 258, 275
Libbey-Owens-Ford Glass Co., 289, 296
Liddell, R. W., 289, 296
Liffaievitch, L. I., 299, 322
Lighthipe, C. H., 302, 306, 323, 325
Lober, F., 290, 296
Lockheed Aircraft Corp., 290, 296
Lode, A., 286, 295
Loebel, Z. C., 78, 95
Loewenstein, L., 283, 294
Long, B., 287, 288, 295
Lontz, J. F., 246, 272, 278
Lorand, E. J., 259, 260, 275, 276
Lowenberg, K., 304, 324
Lowy, A., 256, 275
Lubman, N. M., 44, 45, 49, 54–58, 62, 86, 93, 301, 323
Luchinskii, G. P., 283, 294
Luckenbach Chemical Processes, Inc., 262, 276
Luckenbach, R., 262, 276
Luisada, A. A., 313, 328
Lüdtge, 163
Lüers, H., 180, 182
Lutz, G., 262, 277
Lytle, W. O., 288, 295

MacAfee, M. W., 273, 281
MacAndrews and Forbes, 217, 224, 232, 239, 240, 241
Macarthur, A., 305, 325
Mack, J., 312, 328
Maguire, M. J., 289, 296
Mahoning Mining Co., 269, 279
Maibaum, D., 89, 96
Maier, C. G., 2, 4, 8, 25
Malozemoff, P., 273, 281
Malss, H., 130, 136
Maltepe, A. H., 43, 49
M. & P. Colloid Stabilizers, 222, 240
Mannes, L., 304, 324
Manville Jenkes Co., 244, 274
Marangoni, C., 159, 162, 163, 165, 167–170
Mareelin, A. *See* Mareelin, R.
Mareelin, R., 156, 157
Mars Confeetion, Ltd., 286, 295
Marsh, R. D., 285, 295
Marshall, J. R., 302, 323
Martin, R. B., 245, 275
Martini, L. P., 109, 113
Matalon, R., 30, 48, 72, 94, 111, 113
Matheros, R. R., 215, 239
Mathias, H. R., 300, 322
Matsuura, N., 293, 296
Matthews, F. J., 299, 321
Mattin, H. E., 237, 242, 283, 294
Maust, E. J., 246, 272, 278
Maxwell, J. C., 139
May, J., 222, 240
McBain, J. W., 33, 48, 78–81, 95, 96, 291, 296, 309, 326
McCraeken, J. A., 222, 240
McCullough, E. W., 258, 275
McCully, R. E., 99, 104, 112, 116, 135
McElroy, W. D., 11, 26, 188
McGauley, P. J., 274, 281
McIntire, O. R., 290, 296
McKenna, W. J., 247, 281
McMurray, L. L., 271, 272, 280
McNab, S. G., 304, 324
McNulty, G. M., 301, 322
Meade, G. P., 313, 328
Mearl Corp., 283, 294
Meiklejohn, G. T., 3–5, 25
Melsens, 9, 25
Mensbrugghe, G. L. van der, 21, 151, 163, 168, 170
Mentzer, C. T., 262, 277
Mergen, S., 115, 135
Merrill, R. C., 63, 65–68, 94, 100, 107, 108, 111, 112
Metal Recovery Co., 245, 258, 259, 262, 264, 275–277
Metyushev, B. D., 90, 96, 300, 322
Meyer, E. A., 300, 322
Meyer, J. B., 300, 303, 322, 324
Meyer, L. S., 289, 296
Meyer, W., 179, 182
Micaelli, O., 83, 96
Micafil, A. G., 286, 295
Michaelis, 197, 238
Michelson, 153
Mid-Continent Petroleum Corp., 302, 323
Migray, E., 236, 242
Miles, G. D., 40, 48, 64–67, 70, 71, 94, 103, 105, 112, 148, 150
Miller, G. E., 302, 323
Miller, J. M., 16, 48
Miller, R. J., 255, 275
Milum, V. G., 91, 97
Minerals Separation American Syndicate (1913) Ltd., 258, 262, 275, 277
Minerals Separation, Ltd., 245, 258, 274, 275
Minerals Separation North American Corp., 245, 246, 258, 262, 269, 271–273, 275–280
Minimax, Ltd., 215, 224, 239, 240
Mirčev, A., 34, 36, 48, 299, 322
Mischke, W., 40, 49, 78, 95
Mitchell, H. S., 83, 96
Mit'kevich, G. P., 122, 129, 135, 136
Mitsui, S., 77, 95
Miyake, Y., 53, 93
Modiano, F., 302, 323
Moffett, F. T., 63, 65–68, 94, 100, 107, 108, 111, 112
Mohr, W., 91, 97
Moilliet, J. L., 236, 241
Mokrushin, S. G., 187, 888
Money, G. J., 215, 239
Monsanto Chemical Co., 318, 328
Monson, L. T., 308, 326
Morash, N., 244, 274
Morgenstern, S., 303, 324
Morris, R. C., 300, 304, 322, 324
Morrison, R. I., 80, 96
Morrisroe, J. J., 67, 94
Morrow, R. W., 310, 327
Mortenson, M., 42, 49
Morton, R. J., 271, 280
Moyer, S. P., 271, 280
Muller, 189, 238
Munters, C. G., 290, 296
Muralo Co., 302, 323

Nagel, K., 262, 276
Nakagaki, M., 46, 49, 55–57, 59, 80, 84, 93, 94, 96
Nakamuta, M., 30, 31, 48
Napier, D. H., 3, 4, 25
National Aluminate Corp., 307, 308, 313, 315–317, 325, 328
National Aniline Chemical Corp., 308, 325
National Chemical Products, 260, 276
National Foam System, Inc., 215, 218, 230, 231, 239, 241

National Oil Products Co., 301, 302, 305, 308, 323, 324, 326
Naudet, M., 83, 96
Nelson, R. C., 302, 323
Neumann, S., 312, 328
Neuville, F., 222, 240
Neville, H. A., 32, 48, 168, 170
Newhall, R. G., 67, 94
Newitt, D. M., 3, 4, 25
New Jersey Zinc Co., 269, 279
Ninol, Inc., 246, 272, 278
Nissen, B. H., 180, 183
Nixon, A. C., 304, 305, 311, 324, 327
Noll, A., 40, 49
Nopco Chemical Co., 306, 325
Norring, O., 300, 322
Northwest Magnesite Co., 269, 278
Novikov, N. V., 76, 80, 89, 95
Nutting, G. C., 159, 169
Nye, J. F., 8, 25, 68, 94

Oakley, H. G., 305, 321
Obuchow. *See* Obukhov
Obukhov, E., 125, 126, 129, 136
O'Connell, H. E., 43, 49
Oehman, V., 91, 97
Oil Well Chemical and Materials Co., Inc., 306, 325
Oliver Iron Mining Co., 271, 280
O'Meara, R. G., 272, 280
Osterloh, R. H., 306, 325
Ostwald, Wo., 44, 49, 80, 96, 130, 136, 171, 173, 178, 181–183
Owens-Illinois Glass Co., 288, 295

Pacicot, P. A., 302, 323
Pacific Coast Borax Co., 273, 281
Pankhurst, K. G. A., 65, 66, 68, 80, 86, 94
Paquin, M., 227, 228, 236, 241, 242
Paquot, C., 71, 91
Parlow, R., 133, 136
Patek, J. M., 259, 275
Patentirtes Schaumlöschverfahren Perfect Ges., 214, 239
Patrick, W. A., 168, 170
Patterson, D. W., 262, 276
Pattle, R. E., 6, 9, 25, 36, 48, 80, 87, 96
Pearce, J. A., 116, 135
Pearson, E. P., 273, 281
Pedersen, C. J., 300, 322
Perkins, C. L., 215, 261, 275, 276
Perkins, E. C., 273, 281
Perri, J. M., 38, 48, 79, 84, 95, 171, 180, 182, 196–200, 219, 231, 238, 239, 241
Perrin, J., 155–157, 175, 182
Peter, H., 103, 109, 112
Peter, P. N., 129, 136
Peterhans, E., 3–6, 25
Peters, D., 78, 79, 95
Peterson, E. C., 247, 281
Peterson, H. B., 200, 204, 238
Petrolite Corp., Ltd., 308, 326
Pettyjohn, E. S., 43, 49
Phelps, D. S., 262, 272, 277, 280
Phillips, W. B., 215, 239
Phillips Petroleum Co., 301, 323
Phosphate Recovery Corp., 246, 269, 272, 278
Pickens, R. A., 246, 271, 280
Pittsburgh Corning Corp., 288, 295
Pittsburgh Plate Glass Co., 288, 295
Plateau, J., 9, 19–28, 30, 31, 47, 48, 50, 51, 63, 68, 77, 93–95, 104, 106, 113, 120, 131, 135, 136, 151, 157, 159, 161, 168, 169
Pokhil, P. F., 85, 96
Pool, W. O., 246, 261, 262, 272, 276–278
Popova, M. I., 283, 295
Potash Company of America, 246, 273, 280
Potgieter van Aardt, J. H., 260, 276
Powell, R. F., 260, 261, 276
Preston, W. C., 100, 107, 112, 160, 161, 169
Price, F. H., 291, 296
Process Engineers, Inc., 312, 327
Proseh, W., 173, 182
Pure Oil Co., 301, 323
Pye, D. J., 273, 281
Pyle, C., 306, 325
Pyrene, 218, 221, 230, 231, 236, 237, 239–242
Pyrene-Minimax Corp., 221, 222, 225, 228, 237, 240–242

Quaedvlieg, M., 309, 326
Quigley, C. G., 262, 277
Quincke, G., 86, 96, 165, 166, 170

Raffold Process Corp., 313, 328
Rafton, H. R., 313, 328
Raison, M., 72, 94, 111, 113, 175, 182
Ralston, A. W., 246, 261, 262, 272, 276–278, 308, 311, 325, 327
Rampacek, C., 271, 279
Rathman, R., 287, 295
Ratzer, A. F., 229, 231, 236, 237, 241, 242
Rawling, R. G., 305, 324
Ray, P. A., 262, 277
Rayleigh, J. W. S., 139, 144, 162–164, 168, 170
Rebinder, P. A., 29, 31, 32, 46–48, 54–56, 66, 71, 75, 77, 80, 81, 93, 95, 168, 169, 170
Reed, R. M., 304, 324
Reese, J. E., 259, 260, 275, 276
Refining, Inc., 301, 323
Rehbinder. *See* Rebinder
Reid, J. D., 134, 136
Reid, M., 116, 135
Reid, R. C., 268, 277
Reidelsberger, W., 227, 228, 236, 241, 242
Reilly, Peter C., 256, 258, 275
Reinold, A. W., 141, 144–147, 150–155, 157
Rell, C. N., 309, 326
Remy, H., 4, 5, 25
Retzsch, C. E., 306, 325
Reutenauer, G., 65, 71, 91, 94
Reynolds, 36, 42
Rheem, W. S., 215, 239
Rhodes, F. H., 262, 276
Rhom and Haas Co., 302, 323
Rhumbler, L., 132, 136
Rice, J. A., 289, 295
Richardson, A. S., 100, 107, 112, 160, 161, 169
Richardson, G. A., 80, 91, 95, 97
Richardson, R. W., 303, 323
Richardt, O. C., 40, 48, 91, 97, 98, 109, 110, 112
Rickenbacher, W., 147, 150, 154, 157
Ries, E. D., 160, 169
Ritter, W., 83, 96
Riverside Cement Co., 268, 277
Roberts, E. S., 274, 281
Robinson, E. A., 308, 326
Robinson, H. E., 83, 96
Robinson, J. V., 33, 45, 48, 81, 87, 90, 96
Rodewald, H. J., 32, 48
Rollins, F. S., Jr., 308, 326
Rona, 197, 238
Rosen, R., 311, 327
Ross, J., 40, 48, 64–67, 70, 71, 94, 103, 105, 112, 148, 150
Ross, S., 34, 41, 44, 45, 47–49, 57, 80, 81, 83, 87, 89, 91, 94–96, 103, 105–107, 110, 112, 113, 117, 135, 169, 170, 180
Rowe, V. K., 319, 328
Roxana Petroleum Co., 215, 239
Rozenfel'd, L. M., 126, 127, 136
Rücker, A. W., 141, 144–147, 150–155, 157
Rummler, H., 304, 324

Ruska, H., 181, 183
Ruth, J. P., Jr., 261, 276
Ruyssen, R. G., 76, 95
Ryznar, J. W., 52, 93

Sabetay, S., 71, 94
Sachs, C. C., 290, 296
Sadgopal, 107, 113
Sair, L., 287, 295
Sameshima, J., 30, 31, 48
Šandera, K., 34, 36, 48
Sanders, V., 288, 295
Sandoz, Ltd., 309, 326
Sasaki, T., 36, 39, 48, 55, 56, 61, 77, 87, 88, 90, 93–97
Satterly, J., 294, 296
Sattler, J., 304, 324
Sauer, E., 44, 49, 80, 95
Savitskaya, E. M., 7, 25, 46, 49, 71, 94, 126, 127, 136
Sayre, R. E., 245, 258, 259, 261, 275, 276
Schacht, F., 300, 322
Sachacht, F., G. m. b. H., 303, 324
Scheflon, L., 237, 242
Scheye, H., 299, 322
Schiebl, K., 123, 135, 294, 296
Schilling, K. F., 246, 272, 279, 280
Schlachter, A., 41, 49
Schmalfuss, H., 129, 136
Schmidt, A., 300, 303, 322
Schmidt, K., 222, 240
Schnabel, R., 224, 240
Schneider, R. B., 303, 323
Schnurmann, R., 7, 25, 134, 136
Schoenberg, G., 237, 242
Scholler, K., 304, 324
Schönbein, 12
Schroeder, 189, 238
Schuster, K., 40, 49
Schütz, F., 33, 48, 54, 55, 76–78, 80, 93, 95, 168, 170, 176, 179, 181–183
Schwab, J. L., 9, 25
Schwarz, A., 262, 276
Schwarz, R., 110, 113
Scott, R. B., Jr., 310, 327
Seemann, W., 4, 5, 25
Segebrecht, E. W., 246, 272, 278
Segessemann, E., 301, 323
Seitz, W., 308, 326
Self, E. S., 306, 325
Separation Process Co., 268, 277
Severn, G. W. C., 286, 295
Shedlovsky, L., 103, 105, 112, 148, 150
Shell Development Co., 300, 304, 305, 309–311, 322, 324, 326, 327
Shelton, K. F., 273, 281
Sherertz, J. R., 246, 273, 280
Shipp, J. H., 300, 322
Shkodin, A. M., 77, 95, 132, 133, 136
Shorter, S. A., 168, 170
Showalter, J. C., 301, 305, 322, 321
Sibree, J. O., 130, 136
Sicard, P., 65, 71, 91, 94
Sidorova, E. E., 81, 92, 96
Sieburg, E., 98, 108, 109, 112
Sichr, A., 109, 113, 116, 118, 123, 124, 135, 173, 179, 180, 182
Siems, H. B., 246, 269, 272, 278
Simon, E., 290, 296
Simonis, H. S., 189, 238
Sinnicks, F. S., 261, 276
Sinsheimer, J. G., 38, 48
Sirks, H. A., 91, 97
Skopintsev, N. A., 179, 182
Slater, G., 288, 295
Sloviter, B., 198, 238
Smirnov, V. A., 44, 49, 91, 97
Smirnova, A. M., 29, 47
Smith, C. C., 245, 275
Smith, C. S., 8, 25
Smith, H. G., 306, 308, 309, 325, 326
Smoluchowski, M., 146
Soc. Saint-Gobain, Chauny & Cirey, 288, 295
Socony Vacuum Oil Co., 309, 311, 326, 327
Sokal, E. C., 304, 324
Solberg, T. A., 313, 328
Spellmeyer, E. F., 307, 325
Spencer, G. L., 313, 328
Spencer, H. C., 319, 328
Spengler, O., 179, 182
Stacey, M., 181, 183
Stackhouse, E., 6, 25
Standard Brands, Inc., 302, 323
Standard Oil Companies, 219, 220, 239, 240, 284, 295, 300, 322
Standard Oil Development Co., 223, 240, 289, 295, 300, 301, 304–306, 308–312, 322–327.
Stanek, V. L., 299, 322
Stanley, E., 300, 322
Stanley, H. M., 261, 276
State College of Washington Research Foundation, 269, 278
Steibelt, W., 303, 323
Steiner, A., 44, 49, 80, 96
Stevens, J. L., 261, 276
Stewart, A., 305, 325
Stewart, E. L., 220, 240
Sthamer, E. and R., 79, 95, 224, 225, 236, 240, 241
Stiepel, C., 98, 111, 112
Stokes, A. J., 29, 47
Stokes, E. B., 272, 280
Stolyarova, R. K., 303, 323
Stone, I., 108, 109, 113–116, 135, 171, 180, 182
Strauch, C. B., 285, 295
Strelzoff, S., 274, 281
Suchowolskaja. *See* Sukhovolskaya
Sukhovolskaya, S., 32, 48, 51, 61, 62, 72–74, 93
Sullivan, W. L., 271, 280
Sulman, H. L., 245, 274
Sun, Shiou-Chuan, 76, 95, 133, 136, 254, 257, 261, 275
Svenska Cellulosa Aktiebolaget, 289, 296
Swenson, T. L., 313, 328
Swift, C. K., 232, 241
Swift & Co., 291, 296
Swift & Co. Fertilizer Works, 246, 269, 272, 278

Taggart, A. F., 34, 48, 63, 75, 94, 95, 243, 244, 248, 251, 252, 256, 263–266, 274, 275, 277
Talmud, D., 32, 48, 51, 61, 62, 72–74, 80, 81, 93, 94, 96
Tandberg, J. G., 290, 296
Tarassuk, N. P., 80, 95
Tartaron, F. X., 271, 272, 279, 280
Taylor, T. C., 75, 95, 251, 275
TeGrotenhuis, T. A., 289, 296
Teitelbaum, B. Ya., 45, 49, 81, 84, 85, 91, 92, 96
Terada, R., 30, 48
Texas Co., 220, 240
Textil Kft., 236, 242
Thiele, H., 176, 182
Thodos, G., 301, 323
Thomas, C. A., 215, 220, 239
Thomas, F. W., 290, 296
Thomsen, C., 224, 240
Thomson, J. J., 174, 182
Thomson, W. (Lord Kelvin), 11
Thuman, W. C., 78, 79, 80, 95
Thurman, B. H., 301, 323
Tikhomirova, G. P., 77, 95, 132, 136
Timpson, L. G. M., 218, 225, 228, 237, 239, 241, 242
Todd, W., 236, 241
Todo, N., 75, 95
Trapeznikov, A., 55, 72–75, 93, 94, 159, 160, 169, 170
Trautman, C. E., 81, 88, 90, 91, 96, 309, 326
Treichel, J. B., 224, 240
Tremain, H. E., 304, 324
Tresise, D. J., 230, 237, 241, 242
Tribble, T. V., 302, 323

Trotman, S. R., 39, 48, 80, 91, 95
Trotter, W., 246, 269, 272, 278
Tucker, S., 262, 276
Tucker, W. M., 303, 323
Tunison, B. R., 262, 276
Turner, J. R., 287, 295
Tuve, R. L., 200, 204, 205, 238
Tveter, E. C., 250, 252, 257, 275
Tyrer, D., 312, 327
Tyutyunnikov, B., 77, 95

Ulmer, R., 188
Union Minière du Haut-Katanga Société Congolaise, 262, 277
Union Oil Co. of California, 301, 322
United Products Corp. of America, 217, 239
U. S. Gypsum Co., 289, 295, 296
U. S. Vanadium Corp., 269, 279
Urbain, W. M., 291, 296
Urquhart, G. G., 189, 215, 222, 223, 239–241

Vacuum Oil Co., 213, 238
Vail, J. H., 310, 326
Vana, C. A., 283, 294
Vanderbilt, R. T., Co., 286, 295
Van Deurs, 189, 238
Van Leuven, H. C., 213, 238
Van Leuven, L. B., 213, 238
Van Voorhies, R. L., 304, 324
Vašiček, A., 144
Vaughn, T. H., 72, 94
Venstrem, E. K., 31, 32, 48, 54–56, 66, 77, 80, 81, 93
Verndrel, Etablissements, 283, 294
Verstraete, E. O. K., 76, 95
Vietorin, O., 80, 89, 95
Vishnevskaya, G. R., 80, 90, 95
Vogel-Jorgensen, M., 268, 277
Voitille, J. E., 306, 325
Vondrak, J., 299, 322
Von Blanquet, O., 236, 242
Vorob'ev, N., 299, 322

Wacker, A., 3, 25
Wada, T., 83, 96
Wagener, 189, 238
Wagner, G. H., 6, 25
Wahlin, B. G., 289, 296
Wakefield, C. C., and Co., Ltd., 311, 327
Walker, H. W., 340, 327
Walker, W. W., 217, 239
Wark, E. E., 32
Wark, I. W., 14, 26, 48, 244, 261, 274
Webb, A. M., 244, 274
Weed, F., 262, 277
Weidner, E., 224, 240
Weinaug, C. F., 301, 323
Weiner, N., 246, 273, 280
Weinig, A. J., 246, 268, 269, 273, 277, 280
Weinstein, F. L., 289, 295
Wells, C. H., 243, 274
Wells, P. V., 142, 144, 156, 157
Wells, S. D., 300, 322
Wenström. *See* Venstrem
Werntz, J. H., 261, 276
West Virginia Pulp and Paper Co., 305, 324
Whirl, S. F., 187, 188
White, C. B., 215, 218, 239
Whiteley, A. H., 14, 26, 188
Whitworth, F. T., 245, 275
Wilkerson, E. W., 262, 276
Wilkinson, E. W., 246, 269, 272, 278
Williams, H. E., 114, 135
Williams, J. C., 268, 269, 277, 279
Williams, M. F., 271, 279
Wills, J. H., 67, 94
Wilson, R. E., 160, 169, 258, 275
Winning, C., 304, 324
Winsor, P. A., 71, 94
Winston, J., 289, 295
Wolfenden, E. A., 89, 96
Wolfson, J., 305, 324
Woodhouse, G. E., 259, 275
Woods, W. W., 45, 49, 81, 87, 90, 96
Woodward, H. S., 269, 278
Woolfenden, H. L., 262, 276
Wright, V. W., 220, 240
Wrobel, S. A., 250, 251, 281
Wyandotte, Chemical Corp., 300, 304, 312, 317, 320, 322, 324, 327, 329

Yabroff, D. L., 305, 311, 324, 327
Yaryan, H. T., 262, 276
Young, G. J., 112, 113
Young, H. H., Jr., 305, 324

Zawidzki, J. von, 172, 174, 182
Zhukhovitskii, Y., 305, 324
Zimmer, J. C., 301, 306, 308, 309, 311, 312, 322, 325–327
Zocher, H., 154, 157
Zschacke, F. H., 77, 95

SUBJECT INDEX

A

Abietic acid, 67
  sodium salt, 67, 77
Accumulation in foam, 171
Acetaldehyde, 196
Acetaldoxime, 62
Acetic acid, 39, 50, 53, 61, 87, 90, 303
  calcium salt, 312
  esters, 62, 196, 198, 199, 301
  ferric salt, 51
Acetone, 51, 62, 82, 83, 198
Acidity
  and density, 116
  and foaminess, 58, 63–65, 67, 70, 71, 77–80, 86
Acrylonitrile, 198
Adhesives, 285, 300 ff.
"Aerosol OT." *See* Sulfosuccinates
Aerosols absorption, 283
Agar, 71, 129
Aging, 121, 122, 132, 133, 163–165
Airfoam. *See* Mechanical foam
Albumins, 41, 76, 78–80, 86, 89, 90, 99, 102, 109, 110, 114, 116, 174
Alcohols, 30, 31, 53, 56, 197–199, 303, 304, 317–319
Aldehydes, 258
Alginates, 148
Alkalinity. *See* Acidity
Alkyl aryl sulfonates, 18, 108, 111, 200, 227, 230, 261, 305. *See also* Butylnaphthalenesulfonates
Alkyl phosphates, 112
Alkyl sulfates and salts, 68–71, 108, 111, 115, 134, 177, 305, 306
  in fire-fighting foam, 220
  and soaps, 70
Alkylsulfonic acids and salts, 71, 108, 127, 177, 305
  in fire-fighting foam, 220
  and soaps, 71
Alloys, 89
Aluminum salts, 32, 51, 57, 187, 200, 207 ff
Aluminum sulfate in fire fighting, 189 ff
Amines and their salts, 62, 63, 67, 68, 71, 108, 116, 176
  in fire-fighting foam, 228
  in flotation, 261
  as foam inhibitors, 306
Amyl alcohols, 32, 44, 54–56, 75–77, 85, 86, 91, 112, 173, 186, 187, 256, 303
Analysis, chemical, 283, 303, 313
Angel cake, 286
Aniline, 62
"Antifoam A," 319
Antifoaming agents, 297–321
Antifreeze, 300 ff
Arylsulfonates, 116
Attraction of bubbles in liquid surface, 22

B

Bacteria, 181
Bacteriophage, 181
Barite, 269
Barium chloride, 57, 84
Beating, 9, 33, 40
  and density, 116
  and drainage, 110
  irreproducibility of results, 41
Beer, 1, 30, 40, 81, 86, 91, 98, 99, 104, 109, 112, 116, 133, 180
Benzene, 51, 80, 81, 83, 87, 90, 174
Benzyl alcohol, 57, 85
  derivatives, 259
Betaine derivatives, 71
Bile acids, 78, 176, 179
Black film, 152–157
Bleaching, 284
Boiling, 11, 16, 18, 33, 42, 47, 51–53, 83, 88, 134, 187, 299, 305–308, 312 ff
Bread, 286
Bubble formation, 1–10, 34
  in boiling, 12 ff

Bubble formation—*Continued*
by electrolysis, 17
in porous septa, 6, 7, 34
by rupturing a liquid, 11
at single orifices, 2–6, 34
at a solid wall, 11–18
in superheated liquid, 11, 12
in supersaturated solutions, 10, 11
and surface roughness, 12, 16
Bubble frequency, 4–6
Bubble nuclei, 11, 12
Bubble pressure. *See* Capillary pressure
Bubble shape, 13, 14, 16, 21
in foam, 25
under a monolayer, 74
Bubble volume
changes in foam, 120–122
and concentration, 7
and electric effects, 17
in foam, 117
maximum, 15 ff
minimum, 4
and orifice diameter, 2 ff
and rate of formation, 4 ff, 17
reduction of, 7–10, 41–43
and solid surfaces, 15 ff
and surface tension, 2 ff, 7, 18
and temperature, 3
and tilt of the solid, 3
and viscosity, 3, 4, 7
and wetting, 2, 14 ff
on whipping, 110
Bubbles
lifetime of. *See* Lifetime
in a liquid surface, 21
small, formation of, 7–10, 41–43
Bursting. *See* Rupture
Butter, 83
Butyl alcohols, 36, 37, 55, 56, 198
Butylnaphthalenesulfonates, 7, 46, 71, 127, 228
Butyric acid, 61

C

Calcium chloride, 50, 52, 70, 79, 80, 84
Capillary constant, 15
Capillary pressure
in bubbles, 7, 10, 12, 21, 151
in bubbles in contact, 22
and drainage, 104–107
in drops, 164
on films, 19, 29, 294
in foam, 117–121, 125
in Plateau's borders, 23
and shear modulus, 125
Carbon dioxide, 40, 89, 90, 99, 109, 115, 116, 121, 123, 145, 179, 303
in fire fighting, 189 ff
Carbon disulfide, 6
Carlsberg method, 98
Carry-over, 43, 52
and solid particles, 187
inhibition of, 299 ff
Casein, 76, 80
Castor oil, 5, 299
Catenoid, 19
Cellulose derivatives, 80, 174, 232
Cement rock, 268
Cetyl alcohol, 54, 74, 85, 160, 303
Chalcopyrite, 186
Chemical equilibrium, shift in foam, 171, 174–176
Chemical foam in fire fighting, 189 ff
Chloroform, 50
Choline-esterase, 181
Citric acid, sodium salt, 57
Cleaning of surfaces, 32
Coal, 273
Coalescence of bubbles, 32
in electric field, 149
prevention of, 158, 184
Collapse of foam, 43 ff. *See also* Time of collapse
Color of films, 137–144, 156
Coloration of foam, 76, 176, 178
Compressibility, 117–119, 128
Concrete, 305
Condensation methods of foam formation, 10
Contact angle, 14 ff
advancing, 16
receding, 16
in three-phase foams, 184–188

Copper sulfide, 187
Cottonseed oil, 83, 116
Cream, 90
Cresols, 44, 57, 58, 85, 86, 117, 255, 258
Cutting oil, 300 ff

D

Dearborn treatment, 317
Decanoic acid, sodium salt, 65
Decontamination, 283
"Defoamers," 316, 320
Deformation of bubbles in contact, 22
Deformation of foam, indefinite, 129
Degassing, 284
Density of foam, 41, 110, 114–117, 123
  and electric conductance, 148
  and fire fighting, 200
  and shear modulus, 127
Destruction of foams. *See also* Inhibitors
  chemical, 85, 191, 297–321
  by heat, 134
  by high-frequency vibrations, 133
  mechanical, 133
  mutual, 67, 70, 77, 80
  by radioactivity, 134
  by spark, 134
Detergents, 68–72, 107, 111, 112, 116, 148
  nonionic, 72, 91
  in organic solvents, 83, 91, 116
Diastase, 181
"Diglycol Laurate S" 313, 321
Dimethylaniline, 13
Dispersion methods of foam formation, 1
Dispersity of foam, 117. *See also* Bubble volume
  and aging, 119–121
  at different levels, 122
  in fire fighting, 200, 201
Displacement in surface layer, 85–87, 197
Dolomite, 187
"Dow Corning Antifoam AF Emulsion," 319
Drainage of foam, 27, 98–112, 116, 160, 180
  and concentration, 101, 108
  and electric effects, 154
  and environment, 107
  equations, 102, 103
  in fire fighting, 204, 205
  and foam persistence, 98, 111, 169
  measurement, 98–102
  mechanism, 104–107, 156
  and viscosity, 106, 110
Drilling mud, 301, 306 ff
Drug application, 285
Dust suppression, 291
Dyes, 80, 84, 155, 176, 178
Dyeing, 284, 303
Dynamic coagulation, 38, 47
Dynamic method, 35

E

Eggs, 91, 116
Elaidic acid, sodium salt, 66
Elasticity of films, 81, 162, 163
Elasticity of foam, 125–128
Elastomer foams, 289
Electric conductance, 145–149, 153
  and foam density, 148
Electric double layer, 17, 146, 154, 155, 169
Electric effects, 17, 18, 149
Electrolysis, 17
Electrolytes, effect on foam, 56, 67, 70, 73, 74, 79, 80, 84, 129
  entrainment by foam, 173
Electroösmosis, 147, 152
Emulsions, 75, 76, 80, 85, 87, 90, 91, 299, 301
  of gas in liquid, 1, 11, 83, 115, 117, 158
Enzymes, 180, 291
Ethanol, 6, 7, 32, 46, 50, 55, 59, 77, 82, 84, 85, 197, 198
Ether (diethyl), 5, 39, 50, 51, 81, 82, 86, 90, 196
Ethers, 196, 198, 199
  in flotation 260
Ethylamine, 62

Evaporation retarded by foam, 223, 282
Expansion factor, 114, 200

F

Fermentation, 300 ff
Fibrin, 291
Figure of Merit, 208–210
Film formation, 19, 20, 27 ff
Films between bubbles, 22 ff
  as catenoids, 19
  lifetime of, 27 ff
Fire-fighting foam, 189–238
  for alcohols, etc., 197
  burnback test, 191
  chemical, 189
    composition of charges, 191–193
    stabilizers, 213–223
  covering quality, 207
  expansion, 194, 200 ff
  Figure of Merit, 208–212
  mechanical, 190, 193
    stabilizers, 223–238
  rate of application, 195, 196, 202, 204
  rating, 210
  stability, 205–207
  specific gravity, 200–202
  and temperature, 201
  viscosity, 203–205, 231
  volume, 194, 200
Flotation, mechanism, 185, 248
Flotation collectors, 244 ff
Flotation frothers, 71, 74, 76, 244 ff
  composition of, 250 ff
  and frothing collectors, 249, 261
  properties of, 250
Flotation machines, 41, 263–268
Flotation modifiers, 244 ff
Flotation promoters, 244 ff
  composition of, 253
Fluorite, 269
Flux, 282
Foam height, 35. *See also* Foam volume
Foam index, 99
Foam number, 38, 98, 200
Foam rubber, 289
Foam power, 100
Foam tower, 171
Foam volume, 36
  on boiling liquids, 42, 51, 52
  and bubble diameter, 43
  and concentration, 69, 70–72
  and liquid amount, 36
  and molecular weight, 65, 70
  and rate of gas flow, 36, 42
  and temperature, 43, 69, 91
"Foamacide L" and "S", 317, 320
"Foamex," 320
"Foamglass," 287
Foaminess as a physical quantity, 27, 37, 50
Foaming liquids, classification of, 168
Foaming power, 115
Formation of foam, 1–22
  by agitation, 38 ff
  ease of formation and stability, 33, 42
  on hot liquids, 158
  and molecular weight, 68
  pneumatic method, 33 ff
Formic acid, 61
Fractionation by foam, 78, 102, 171, 176–180, 291
  coefficients of, 177
Froghopper, 282

G

Galena, 186, 187
Garnet, 271
Gas absorption, 283
Gas analysis, 293
Gas composition, 89, 90
  and drainage, 109, 110
  and foam fractionation, 179, 180
Gas diffusion between bubbles, 120, 121
Gas flow rate, 293
Gas pressure in foam, 117
Gelatin, 39, 76, 78, 80, 86, 89, 91, 109, 115, 187, 200, 292
  deaminated, 78
Germanium compounds, 310
Glass, 89
Glass foam, 287

Glue, 39, 44, 80, 212 ff, 302 ff
Glycerol, 46, 50, 57, 59, 68, 83, 107, 116
  in fire-fighting foam, 223 ff
Glyceryl monolaurate S-547, 314
Glyceryl monoricinoleate S, 314
Glycol ethers, 72, 257
Glycolic acid esters, 259
Glycols, 41, 57, 87, 116, 196, 304
Graphite, 274
Gums, vegetable, 68, 80, 110, 115

H

Half-life, 100, 104, 205
Halite, 273
Hardness of water, 292
Heptanes, 51
Heptanoic acid, 61, 62, 80, 115
Heptanols, 55
Hexanoic acid, 61
  salts, 67, 78
Hexanols, 36, 55, 76
Honey, 91
Hormones, sex, 181
Humic acid, 44, 80
Hydrocarbons, 80, 81, 84, 91–93, 191
  chlorinated, 311
  fluorinated, 311
Hydrolysis, 175
Hydroperoxides, 259
Hydrostatic pressure of foam, 123

I

Ilmenite, 271
Incorporation of gas in liquid, 42, 64, 65, 70, 88
Inhibitors of foam, 84, 87, 99, 297–321. *See also* Mixtures
  for acid and alkali, 300
  in boiling, 18, 85, 299, 305, 308, 312, 313, 316, 317
  as emulsions, 90, 299
  in food industry, 302
  and molecular weight, 303
  solid, 312, 313
Insecticide, 283
Interference of light, 137–144
Iron ores, 270
Iron salts, 57, 187, 213 ff
Isoelectric point, 78, 79

K

Ketones, 198, 199, 259
Kyanite, 271

L

Lactic acid, 61
  potassium salt, 215
Lactose, 116
Lanthanum chloride, 79
Lauric acid, 74
  calcium salt, 67
  esters, 71
  miscellaneous salts, 67, 176
  potassium salt, 65, 91, 176
  sodium salt, 30, 63–65, 67, 107, 108, 111, 133, 160, 176–178, 291
Lead sulfide, 187
Leather dressing, 304 ff
Lecithin, 110, 129
Licorice root, 214, 224
Lifetime of bubbles, 31 ff, 46, 51, 54–56, 62 ff
Lifetime
  of foam, 37
    and bubble diameter, 31, 37, 47
    and chemical structure, 74, 75, 251
    comparison of different methods, 46, 47, 52, 55, 59, 63, 64, 66, 77, 88
    and concentration, 51, 52, 56, 58, 61, 63–65, 75
    and drainage, 98, 111, 112, 169
    and ease of formation, 33
    and environment, 29–33, 46, 47, 57, 66, 76, 81
    and homologous series, 75, 82
    and solubility, 75, 84, 89, 90, 251, 258
    and surface concentration, 72, 85
    and surface tension, 51, 63, 66
    and temperature, 65, 74, 91–93, 112
    and vessel dimensions, 36, 39, 47
  of gas in foam, 44, 81, 112
  of growing bubbles, 29

Lifetime—*Continued*
of liquid in foam, 104, 112
of single films, 27 ff, 63
and cleanness, 32, 33
and film area, 30, 63, 72
Light transmission, 144
Limestone, 187
Linoleic acid, sodium salt, 66, 107
Linseed oil, 83, 299
Lipase, 181
Lubricants, 45, 47, 88, 90, 91, 106, 110, 111, 116, 302 ff
Lyotropic series, 51

M

Machines for foam production, 10, 222. *See also* Flotation machines
Magnesite, 269
Magnesium chloride, 52, 70
Magnesium sulfate, 57
Malt, 122, 129
Manganese ores, 270
Matches, 285
Maximum of persistence, 32, 51–61, 66, 68, 69, 72, 74, 77, 81, 82, 176
elimination of, 75, 85
and molecular weight, 54, 61, 75
theory of, 75, 76, 165–167
in three-phase foams, 186
Mechanical foam in fire fighting, 190
Mechanical properties of foam, 114–134
of surface films, 85, 86
Mercury, 9, 32
Methanol, 51, 55, 81, 83–85, 92, 93, 197, 198
Methylaniline, 63
Milk, 80, 91, 294, 313
Minimum concentration of foaming, 68, 77
Mixtures, 83–88
of alcohols, 56
and density, 116
and drainage, 112, 116
of inorganic salts, 52
of nonfoaming substances, 71
of organic substances, 59, 77, 80, 81
Mixtures—*Continued*
of proteins and alcohols, 197
of soaps, 67
of soaps and builders, 67
of soaps and other organic substances, 71
Modulus of compression, 128
Modulus of elasticity, 128
Molybdenite, 186
Monodisperse foams, 34, 46, 47
Monolayers. *See* Unimolecular films
"Monsanto AE," 318
Movement of foam in tubes, 123, 130, 208
Multicellular concrete, 288
Myristic acid, 74, 85
calcium salt, 67
potassium salt, 65, 91
sodium salt, 64, 65, 67, 107

N

"Nalco," 315–317
Naphthylamines, 44, 62
Nitrobenzene, 51, 62, 81, 83, 84, 92
Nonanoic acid, 61, 85
"Nopco," 316, 321
Nuclei, gas, 11, 12, 16, 18

O

Octanoic acid, 61, 62
Octanols, 55, 76, 256, 303
Oils
animal, 100, 110
as foam inhibitors, 299–301
Oils
vegetable, 83, 100, 110
as foam inhibitors, 299–301
Oleic acid, 77, 80, 87, 90, 160, 187
ammonium salt, 68, 121
esters, 72
miscellaneous salts, 67, 68, 80
potassium salt, 65, 91, 155, 156, 178, 306
sodium salt, 31, 64–67, 77, 78, 80, 107, 108, 111, 132, 146, 152–154, 165, 173, 175–178, 291, 292
Olive oil, 80, 83, 116
Opacity of foam, 144

Organic solvents, 80–83
Oscillating jet, 163

P

Paint manufacture, 300 ff
Palmitic acid, 74
  calcium salt, 67
  esters, 72, 160
  potassium salt, 178
  quaternary ammonium salt, 67
  sodium salt, 41, 65, 67, 107, 178
Paper coating mixes, 114, 303 ff
Paper making, 300 ff, 315
Paraffin oil, 81, 83
Paraldehyde, 62
Particle size in three-phase foams, 186
Peanut oil, 83
Pectin, 76
Pentanone, 62
Pepsin, 181
Peptone, 76, 109, 115, 229 ff
Perforated plate method, 40, 41, 64, 69, 111
Persistence. *See* Lifetime
Petroleum, 90
Petroleum fires, 189 ff
pH. *See* Acidity
Phenol, 57
Phenols, 224, 258
  chlorinated, 59
Phosphate rock, 269
Phosphoric acid
  esters, 308, 321
  salts, 312
Phthalic acid esters, 302
Pine oil, 76, 254, 300
Piperidine, 84
Plant extracts in fire fighting, 221
Plastics foams, 289
Plateau's border, 23
  and drainage, 104–107, 132
Pneumatic method, 33, 54, 57, 61 ff
Poisson ratio, 128
Polyamides, 18, 85, 306–308, 316
Polydispersity, 121
"Polyethylene Glycol 400 Monolaurate," 314
Polyethylene glycols, 83, 116, 225
Potassium bromide, 51
Potassium chloride, 51, 52
Potassium ferricyanide, 51
Potassium hydroxide, 51
Potassium nitrate, 50, 52, 146, 154
Potassium phosphate, 67
Potassium pyrophosphate, 67
Potassium thiocyanate, 51, 57
Potato juice, 118, 123, 179
Pour test, 40, 63–67, 70, 72, 78, 91
Pressure, internal, 117–120
Pressure effect on drainage, 109
Priming, 43. *See also* Carry-over
Probability theory of foaminess, 44, 46, 131
Propionic acid, 61
Propyl alcohols, 55, 82, 99, 197, 198
"Propylene Glycol Monolaurate S-1003," 314
Protein hydrolysates, 90, 121, 126, 130, 144, 148, 180
  in fire fighting, 189, 193, 200 ff
Proteins, 40, 78–80, 91, 129, 131, 160, 180
  in fire fighting, 197, 203, 215 ff
  in food, 286
Pulmonary edema, 313
Pure liquids, 50, 83, 165
Purification by foaming, 176–181
Pyrotechnics, 285

Q

Quaternary ammonium salts, 32, 67, 71, 133
  as foam inhibitors, 308
  in fire fighting, 225

R

Radius of molecular action, 151, 152
Rayon spinning baths, 244
Rennin, 181
Residual head, 99
Resilience, 132
Reynolds number, 36, 42
Rhodocrosite, 270
Ricinoleic acid, sodium salt, 66, 67
Rigidity, 129, 131
Rise of foam, rate of, 37

Rupture of foam films, 130
mechanism of, 44, 131, 132, 161–163
velocity of, 133

S

Salicylic acid methyl ester, 63
Salmine, 79
Saponins, 33, 76, 77, 101, 108, 109, 115, 116, 123, 125, 127, 129, 131, 132, 148, 160, 168, 172, 173, 291
in fire fighting, 189, 212 ff
in food, 286
Saturated solutions, 50, 165
Scheelite, 269
Sea water, 53, 179
Sensitive purple, 141
Separation by foam, 177, 178
"SF-96," 320
Shaking, 38 ff, 53 ff
dependence of results on procedure, 39, 42, 83, 87, 90
and Reynolds number, 42
standard, 40
Shear modulus, 124–128, 204
Silica, 272
Silicon compounds, 88–90, 309–310, 319, 320
Slags, 89, 158
Soap, 63–68
"acid," 65, 77
in aqueous glycerol, 31, 63, 68, 120, 132, 146, 153, 154, 156
detergent action, 294
drainage, 107, 111
in fire-fighting foam, 218 ff
as foam inhibitor, 305
mixtures, 67
and organic additions, 70, 71, 77, 80
and pH, 63, 65, 67
Soap bubbles, 1
chains, 127
formation, 20
Sodium bicarbonate, 189 ff
Sodium carbonate, 50–53, 312
Sodium chloride, 52, 57, 67, 70, 79, 80, 84, 107, 187
Sodium hydroxide, 51–53, 187
Sodium nitrate, 84
Sodium silicate, 112
Sodium sulfate, 51–53, 57
Solubility
gas in liquid, 89, 90, 109, 121
liquid in liquid, 75, 84, 93
Sorbitan esters, 314
Sound, 294
Soybean proteins, 79, 84, 180, 193, 201 ff, 287
Span, 314, 315
Specific surface of foam, 7, 90, 121
Sphalerite, 186
Spittle insects, 282
"SS-66," 319
Stability of foam in acid, 71. *See also* Acidity
Stabilization of foam by powders, 65
Stable foams, 67, 68, 83
Starch, 313
Static coagulation, 38, 46, 47
Steam bubbles, 12, 16 ff
Stearic acid, 80, 81, 85, 160, 301
esters, 74, 286, 301
miscellaneous salts, 67, 207, 305, 306
potassium salt, 130, 178
sodium salt, 65, 70, 107, 178, 305, 306
Stiffness, 41
Stratified films, 155
Structure of foam, 23, 89, 105
Structure of lamellae, 146
Sucrose, 62, 68, 116, 129
Sugar juice and molasses, 36, 123, 133, 179, 291, 294, 299 ff
Sulfate liquor, 109
Sulfide minerals, 268
Sulfite liquor, 44, 91, 217, 225, 289
Sulfosuccinates, 45, 47, 68, 71, 83, 108, 111, 127, 305
Sulfur, 274
Supersaturated solutions, foam from, 10, 11
Surface conductance, 146
Surface roughness, 12, 16, 130, 292
Surface tension
and bubble shape, 21, 74
and bubble volume, 2 ff, 7, 18
and chemical equilibrium, 174
and compressibility, 119

Surface tension—*Continued*
and displacement in surface layer, 86–88
and film thickness, 151
and foam deformation, 124, 127
and foam persistence, 51, 63, 66
and foam structure, 23
of fresh surfaces, 163–167
nonequilibrium, 30, 86, 163–167
and rupture of foam, 130, 131, 134, 161
and surface viscosity, 159
in three-phase foams, 184
Surface viscosity, 158–161, 212, 213
Sylvite, 273
Syneresis, 101

T

Talc, 271
Tannery proteins, 80
Tannin, 68, 80, 313
Temperature
and drainage, 110
and electric conductance, 145
of foam, 168
and foam expansion, 201
and foaminess, 43, 65, 69, 74, 83, 91–93, 112
Ternary solutions, 83–88. *See also* Mixtures
Terpineols, 32, 76, 255
Thickness
of black films, 153–155
of films
determination, 138–144, 146, 153
elementary, 155
and radius of molecular action, 151
at rupture, 30, 132, 168, 169
Thiophene derivatives, 311
Three-phase foams
liquid-liquid-gas, 87, 93
liquid-solid-gas, 65, 181, 184–188, 243–274, 312
Time of collapse, 45, 51 ff
and concentration, 58, 64, 65, 77
and drainage, 111
and electrolytes, 56
and environment, 57, 71
at high temperatures, 207
and size of sample, 46, 111
and solubility, 93
and surface tension, 167
Tocopheryl phosphate salts, 30, 71, 132, 152
Toluidines, 38, 47, 62, 63
Total head, 99
Triethanolamine as solvent, 45, 83, 87
Two-bubble method, 32

U

"Ucon," 318
Undecylenic acid, sodium salt, 65, 78
Unimolecular films, 61, 72–74, 85, 159, 160
Urine, 36, 293

V

Valeric acid, 61
Vertical films, stability of, 163
Viscosity
of foam, 129, 130, 203, 204
and foam formation, 158

W

Wetting, 2, 3, 14 ff, 133, 184–188
Whipping. *See* Beating
Wine, 109

XYZ

Xanthates, 245 ff
Yeast, 90, 304, 315, 321
Yield stress, 159, 160
Zinc salts, 213
Zinc sulfide, 187

LIBRARY
18 JUN 1954

C. F. T. R. I. LIBRARY, MYSORE.

CHECKED 2008

VERIFIED 2013

CFTRI-MYSORE
2947
Foams: Theory an